nature portfolio

Peer Review File

Interfacial hydride transfer for dehalogenation with water

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript reports the synthesis of a SiH-ZVI material and its application in hydrogenation reactions of several halogenated compounds. In particular, the authors employ comprehensive characterization and theoretical modeling to support a surface hydride-transfer mechanism. Overall, the manuscript is generally well written and supported by extensive data.
One issue that remains unclear is why such material is required. If the purpose is decontamination, the selected contaminants can all be readily degraded by other established materials. Alternatively, the goal may be to establish a new selective hydrogenation pathway that avoids the generation of carbon-centered radicals, but most of the data using florfenicol do not address this purpose clearly. If the intended application is selective hydrogenation for value-added product synthesis, the current text seems to lack adequate supporting data and arguments for this aspect. The authors should clarify the novelty of this material or process before this work is considered for publication.
Additional specific questions are as follows:
(1) Line 13, 30, and other relevant places: The phrase “detoxification and valorization” should be replaced with more appropriate terminology. The manuscript does not provide evidence to support toxicity alleviation, and the valorization discussion appears to distract from the main results.
This also applies to the phrase “bridging the gap between environmental remediation and precision chemical synthesis.”
(2) Line 15 and other relevant places: Is it true that hydrodehalogenation conventionally relies on radical-based interfacial hydrogen transfer? A more common pathway is two-electron transfer followed by protonation.
(3) Line 29 and other relevant places: What exactly does “selective hydrogenation” mean in this context? Selective against what? A clear definition should be provided upfront.
(4) Line36-38: References are required to support the statement regarding the type of process that would lead to H2 cleavage.
(5) Line 38-40: These two sentences need to be rephrased. They do not appear to be consistent with the mechanism/pathway depicted in Scheme 1a, which shows a hydrodehalogenation reaction induced by single-electron transfer rather than by an H radical. In addition, the statement that the “electrophilic nature of H• renders it a poor match for the C–X bond” is unclear. The carbon-centered radical is not formed through “halogen atom abstraction”; rather, it is generated by the release of a halide ion after the substrate captures an electron.
(6) Line 41: Please clarify why this mechanism would lead to poor selectivity. The explanation beginning with “as these intermediates...” does not adequately explain the origin of poor selectivity. In particular, why are dimerization or polymerization considered undesirable side reactions? This point is related to the definition of the optimal outcome of dehalogenation, especially if “selectivity” specifically refers to the replacement of C–X with C–H.
(7) Scheme 1 was not cited in the manuscript.
(8) Line 79: This paragraph reads like a conclusion section. It should be revised to instead present the study’s hypothesis, key methodology, and research logic more clearly.
(9) Line 162: The manuscript should clarify why florfenicol was selected as the model compound. Specifically, was its selection based on environmental relevance, structural features, or a combination of both? Especially given that the broad applicability of the material was tested by common chlorinated hydrocarbons in groundwater.
(10) Line 196: The KIE values larger than one support the involvement of H2O and, subsequently, surface hydride species in the dechlorination/defluorination reactions. However, why do these values also suggest that hydrogen transfer is the rate-limiting step?
(11) Contradictory statements need to be fixed: Line 169 states that “The enhanced activity was most pronounced during the hydrodechlorination stages”, corresponding to a 12-fold increase. However, Line 185 reports that the defluorination rate constants increased by 20-fold. The authors should clarify this apparent inconsistency.

(12) Line 171, the values of “1.7 and 5 times greater” do not match the data presented in in Figure 2c.
(13) Fig. 2f: The figure legends, including labels such as H2O, m/z values, and explanatory notes such as Si-H, should be updated to accurately reflect the synthesis and reactions of SiD-ZVI with D2O.
(14) Line 320: The authors demonstrate the broad applicability of the method using several common chlorinated contaminants. However, many of these contaminants can be readily degraded by other materials, including modified ZVI systems. If the novelty of this study lies in developing a new material for decontamination, the authors should provide a clearer rationale for why such a material is needed for these contaminants and demonstrate its advantages over previously reported materials.
(15) Line 369: The authors should clarify why deuterated acetic acid is considered a valuable product. Does the reported 98% purity meet the requirements for its intended application? In addition, the manuscript should explain the advantages of the SiH-ZVI approach compared with current industrial production methods. As currently presented, the valorization discussion appears somewhat disconnected from the main text. Alternatively, the authors should more clearly emphasize the importance and technical need for the selective replacement of C–X bonds with C–H bonds. Otherwise, the valorization part reads more as an attempt to broaden the impact of the current work, rather than as a component to advance scientific questions.

Reviewer #2

(Remarks to the Author)
Title: Interfacial hydride transfer for sustainable dehalogenation with water

The authors report a mechanochemically activated zero-valent iron (ZVI) platform that, in the presence of trace water and silicate-derived interfacial Lewis’s acid-base pairs, generates nucleophilic Si–$H^{\delta-}$ species to drive highly efficient and regioselective dehalogenation. This platform demonstrates rapid kinetics, water-mediated regeneration of active sites, and practical application in continuous-flow treatment of real contaminated groundwater. It seems interesting and attractive, but there remain several issues of the writing format and mechanistic explanation. Publication should be considered after a minor revision. Specific comments are listed below.

1. Scheme 1. “Interfacial hydride transfer” in the caption should use lowercase “I” (i.e., “interfacial”) for consistency with “conventional hydrogen atom transfer”.
2. In figure 1b. “Rention Time” on the x-axis should be corrected to “Retention Time”.
3. In figure 2g. The label “Transtimmittance” contains a spelling error. Please correct this to “Transmittance”. And the y-axis label incorrectly places the unit outside the parentheses. Please standardize this notation to match journal conventions.
4. In figure 3. The legend “Raman shit ($cm^{-}1$)” in figures d and e contains a clear written error. Please correct this to “Raman shift ($cm^{-}1$); The reaction coordinate on the x-axis of figure f isn’t fully visible, it may be obscured by the graph below. The label “regeneation” in the mechanism cycle contains a spelling error, please correct this to “regeneration”.
5. The manuscript refers to “trace water”, and the actual amount used is 69 μL. Could the authors clarify how this water dosage was determined, and why this specific volume was selected as the optimal condition for surface hydride formation and dehalogenation performance?
6. It would be better to include some introduction and discussion on recently reported modifications of nZVI and ZVI materials, such as sulfidation and latter engineering, which also show good performance on dehalogenation. This may help readers recognize specific applications scenarios of different materials.
7. As ZVI provides electrons, a passivation layer of iron oxides/hydroxides will inevitably form. How does this insulating layer affect the generation of Si–$H^{\delta-}$ over time? Can the Si$H^{\delta-}$-ZVI and other reference materials be regenerated after the ZVI core is completely oxidized?
8. Line 234–240. The authors state that the persistence of the Si–Hδ– signal in the in situ FTIR spectra indicates regeneration rather than stoichiometric consumption of the active hydride species. Could the authors provide quantitative evidence that the FTIR signal intensity truly reflects the concentration of catalytically active Si–Hδ– sites?
9. The proposed mechanism in figure 3i involves the formation of surface-bound Si–Cl/F intermediates during dehalogenation. Could the accumulation of these cleaved halide species on the catalyst surface poison or block the active sites, for example by competitive adsorption or irreversible site occupation?
10. For large-scale sustainable remediation, how does the cost of synthesizing Si-ZVI compare with traditional ZVI material or other widely used iron-based remediation materials?
11. How do groundwater matrices (humic acid, cations, carbonates) influence Si–$H^{\delta-}$ stability?
12. Are there any dissolved silicon species leaching into the solution during the dehalogenation process? What is the chemical stability of the Si shell?
13. While the authors demonstrate high reactivity of Si–$H^{\delta-}$ toward aliphatic C-X bonds (e.g., TCE), it remains unclear whether this interfacial hydride transfer is equally effective for aromatic compounds or PFAS, which have significantly higher bond dissociation energies. Could the authors elaborate on the scope and limitations of their system?

Reviewer #3

(Remarks to the Author)
This manuscript titled “Interfacial hydride transfer for sustainable dehalogenation with water” presents a novel mechanochemically activated zero-valent iron (ZVI) material that enables interfacial hydride transfer for efficient hydrodehalogenation of organic halides. The authors provide compelling spectroscopic, electrochemical, and computational evidence supporting the formation of SiHδ– species and their catalytic role. The work is innovative, well-executed, and has significant implications for both environmental remediation and green chemical synthesis. Therefore, I recommend

publication after all the following issues were well addressed. The comments are listed below.
1.The manuscript describes the synthesis of SiHδ–-ZVI by ball-milling iron powder with sodium silicate and trace water. However, it is unclear whether the metallic Fe0 content of ZVI changes significantly after SiHδ– modification (e.g., due to Fe0 corrosion). Please provide quantitative analysis of the Fe0 content of SiHδ—ZVI and ZVI to support the stability of the electron reservoir.
2.The core-shell structure is mentioned based on HRTEM/HAADF-STEM images (SI Figs. S7–S8). Could the authors provide statistical data or representative measurements of the oxide shell thickness of SiHδ–-ZVI and ZVI? A discussion on how ball milling with silicate and water affects shell morphology of ZVI would strengthen the material characterization.
3.The authors propose that “the metallic Fe core acts as an electron reservoir, which is crucial for stabilizing the electron-rich surface hydride species.” To strengthen this claim, a more direct assessment of the material’s electron release capacity after SiHδ– modification, especially compared to pristine ZVI would be valuable. Please consider adding a brief analysis, for example via Tafel analysis or electrochemical impedance spectroscopy (EIS) measurement to evaluate corrosion potential and charge transfer resistance. This would clarify how SiHδ– modification influences the electron donation ability of the ZVI.
4.In situ FTIR (Fig. 2g) reveals a Si–Cl stretching vibration at 575 cm^{-1} that grows during the reaction, suggesting that chloride released from C–Cl bond cleavage is captured by surface silicon. While the authors show that SiHδ–-ZVI signals persist after reaction (SI Fig. S19), it is not clear whether accumulated Si–Cl species gradually deactivate the active sites over extended operation. It would be valuable to evaluate the chlorine mass balance (e.g., whether Cl^- is fully released into solution or partially accumulates on the catalyst surface). A short discussion on this point would enhance the practical relevance.
5.The proposed regeneration cycle relies on electron transfer from the Fe0 core to regenerate SiHδ–-ZVI. Over extended reaction times, the Fe0 content should gradually decrease. However, the manuscript does not provide any quantitative measurement of the residual Fe0 content after long-term reaction (i.e., measurement of Fe0 content after prolonged reaction). It would be valuable to determine the Fe0 content in the post-reaction SiHδ–-ZVI and compare it with the fresh material. This would directly support the proposed “electron reservoir” role and help evaluate the material’s long-term electron supply capacity.
6.Minor editorial corrections. Page 10: “forlenicol” should be corrected to “florfenicol”. Reference 12: “keteneous catalysis” should be “heterogeneous catalysis”. Figure 2a inset: the unit of kobs is missing; please add (e.g., min^{-1} or h^{-1}). There is a spelling error on page 3 in the Introduction section: “undesira0bl” should be corrected (e.g., to “undesirable”).
7.You report that the electron selectivity (ε_e) of SiHδ–-ZVI in real groundwater is increased by 185 times compared to pristine ZVI (Fig. 4c), whereas in a buffer system the increase is only 6.8 times (SI Fig. 24f). What is the main reason for this large difference?
8.In the TCE dechlorination by ZVIs, you demonstrate the enhancement of electron efficiency (ε_e) by a factor of 6.8–185 and attribute it to the suppression of hydrogen evolution by SiHδ–-ZVI. However, for florfenicol (FF), the most important model pollutant in the manuscript, you only report the rate enhancement factors without presenting the electron efficiency or the extent of hydrogen evolution inhibition. Could you please provide the electron efficiency of SiHδ–-ZVI in the FF system, and the enhancement factor relative to the control groups (Si-ZVI or ZVI)?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
All the previous comments have been properly addressed. I have no further advice.

Reviewer #2

(Remarks to the Author)
The authors have addressed the comments. I would recommend for the publication.

Reviewer #3

(Remarks to the Author)
In the revised Nat. Commun. Manuscript titled, “Interfacial hydride transfer for sustainable dehalogenation with water”, the authors were able to address all of my publication concerns. It is also notable that they were also able to accommodate most of the concerns of the other two reviewers through re-wording and additional figures/text. I believe the revised version to be clearer and more cohesive, therefore now be ready for publication.

Point-by-Point Responses to Reviewers' Comments

We thank the reviewers and the editor for their careful consideration of our manuscript. We were pleased that no fundamental errors or inconsistencies were identified in the work. All suggestions have been incorporated into the revised manuscript and/or supporting information. Below we summarize our responses to the Reviewers' comments (blue text), with revisions to the text in red. The revised parts in the tracked-edits version of the manuscript are identified with yellow highlighting.

Reviewer 1: The manuscript reports the synthesis of a SiH-ZVI material and its application in hydrogenation reactions of several halogenated compounds. In particular, the authors employ comprehensive characterization and theoretical modeling to support a surface hydride-transfer mechanism. Overall, the manuscript is generally well written and supported by extensive data. One issue that remains unclear is why such material is required. If the purpose is decontamination, the selected contaminants can all be readily degraded by other established materials. Alternatively, the goal may be to establish a new selective hydrogenation pathway that avoids the generation of carbon-centered radicals, but most of the data using florfenicol do not address this purpose clearly. If the intended application is selective hydrogenation for value-added product synthesis, the current text seems to lack adequate supporting data and arguments for this aspect. The authors should clarify the novelty of this material or process before this work is considered for publication.

Additional specific questions are as follows:

(1) Line 13, 30, and other relevant places: The phrase "detoxification and valorization" should be replaced with more appropriate terminology. The manuscript does not provide evidence to support toxicity alleviation, and the valorization discussion appears to distract from the main results.
This also applies to the phrase "bridging the gap between environmental remediation and precision chemical synthesis."

Reply: Thanks for this valuable comment. We have revised the relevant statements to be more accurate and avoid ambiguity.

1. In the Abstract (Line 13-14), we revised the sentence to:

   "Reductive dehalogenation of organohalides through hydrodehalogenation with water is critical for environmental and chemical industries."(Page 2, Lines 13-14)

2. In the Abstract (Line 29-31), we revised the sentence to:

   "This work establishes a versatile and sustainable mechanochemical platform for selective hydrodehalogenation of organohalides with water, enabling a direct interfacial hydride transfer pathway that directs the reaction flux towards the target C–H product." (Page 2, Lines 29-32)

3. In the Introduction (Line 36-37), we similarly revise the sentence to:

   "Hydrodehalogenation is a pivotal reaction in both for environmental remediation and synthetic chemistry." (Page 3, Lines 34-35)

(2) Line 15 and other relevant places: Is it true that hydrodehalogenation conventionally relies on radical-based interfacial hydrogen transfer? A more common pathway is two-electron transfer followed by protonation.

Reply: We sincerely thank the reviewer for this suggestion. As the reviewer pointed out, two-electron transfer followed by protonation (a carbanion pathway) and stepwise electron/hydrogen radical transfer (a carbon-centered radical pathway) are two distinct mechanisms in hydrodehalogenation. In the former, the substrate accepts two electrons in a concerted ot sequential manner to form a carbanion, which is then protonated. In the latter, single-electron transfer generates carbon-centered radical intermediates, which subsequently abstract a hydrogen atom from a hydrogen radical (H•).

During the revision, we have revised the relevant statements to summarize both pathways, while distinguishing our direct interfacial hydride transfer ($H^{\delta-}$) mechanism as a third, fundamentally different route, one that bypasses both high-energy carbon-centered radical and carbanion intermediates.

In the Abstract (**Line 14-16**): "Conventional hydrodehalogenation proceeds via electron transfer pathways (e.g., stepwise electron/hydrogen radical transfer, or two-electron transfer followed by protonation), which are often hampered by limited dehalogenation kinetics and selectivity." (Page 2, Lines 14-17)

In the Introduction (**Line 37-43**): "Conventional strategies predominantly proceed via electron transfer pathways that generate reactive high-energy intermediates, either carbon-centered radicals (via single-electron transfer) or carbanions (via two-electron transfer), which are then converted to the hydrogenated product through hydrogen atom abstraction or protonation. However, both pathways are often plagued by limited kinetics and poor product selectivity, as the high-energy intermediates readily undergo undesirable side reactions such as polymerization, coupling, or over-reduction." (Page 3, Lines 37-43)

(3) Line 29 and other relevant places: What exactly does "selective hydrogenation" mean in this context? Selective against what? A clear definition should be provided upfront.

Reply: Thank you for this valuable suggestion. In our work, "selective hydrogenation" refers to the replacement of carbon-halogen (C–X) bonds in organohalides with C–H bonds to form the hydrogenated product. To avoid ambiguity, we revised the description to a more precise term, "selective hydrodehalogenation of organohalides", as follows:

"This work establishes a versatile and sustainable mechanochemical platform for selective hydrodehalogenation of organohalides with water, enabling a direct interfacial hydride transfer pathway that directs the reaction flux towards the target C–H product." (Page 2, Lines 29-32)

(4) Line 36-38: References are required to support the statement regarding the type of process that would lead to H_2 cleavage.

Reply: Thanks for this constructive suggestion. We recognize that the original statement "homolytic H_2 cleavage" was inaccurate for describing H• generation in this system. In the revised manuscript, we have corrected this description and supplemented the relevant reference as follows:

"Specifically, the stepwise electron transfer followed by interfacial hydrogen transfer, where atomic hydrogen radicals (H•), generated via water dissociation, serve as the active species.[6]" (Page 3, Lines 43-45)

(5) Line 38-40: These two sentences need to be rephrased. They do not appear to be consistent with the mechanism/pathway depicted in Scheme 1a, which shows a hydrodehalogenation reaction induced by single-electron transfer rather than by an H radical. In addition, the statement that the "electrophilic

nature of H• renders it a poor match for the C–X bond" is unclear. The carbon-centered radical is not formed through "halogen atom abstraction"; rather, it is generated by the release of a halide ion after the substrate captures an electron.

Reply: We sincerely appreciate the reviewer for this insightful comment. We have revised the description of **Scheme 1a** as:

> "the stepwise electron transfer followed by interfacial hydrogen transfer, where atomic hydrogen radicals (H•), generated via water dissociation, serve as the active species.[6] The uncharged, radical-based nature of H• renders its reactivity fundamentally mismatched with the polar C–X bond, leading to inefficient direct hydrogenation and preferential dimerization into H_2 (**Scheme 1a**)." (Page 3, Lines 43-47)

We also agree that the original phrase "electrophilic nature of H•" was chemically inaccurate. Actually, H• is an uncharged radical species, not an electrophile. Its reactivity is governed by radical pathways (single-electron transfer), which are fundamentally distinct from the polar (two-electron, ionic) character of the C–X bond. During the revision, we have revised the description as:

> "The uncharged, radical-based nature of H• renders its reactivity fundamentally mismatched with the polar C–X bond, leading to inefficient direct hydrogenation and preferential dimerization into H_2 (**Scheme 1a**)." (Page 3, Lines 45-47)

The discussion about the formation of carbon-centered radical have revised as:

> "Conventional strategies predominantly proceed via electron transfer pathways that generate reactive high-energy intermediates, either carbon-centered radicals (via single-electron transfer) or carbanions (via two-electron transfer), which are then converted to the hydrogenated product through hydrogen atom abstraction or protonation." (Page 3, Lines 37-40)

(6) Line 41: Please clarify why this mechanism would lead to poor selectivity. The explanation beginning with "as these intermediates..." does not adequately explain the origin of poor selectivity. In particular, why are dimerization or polymerization considered undesirable side reactions? This point is related to the definition of the optimal outcome of dehalogenation, especially if "selectivity" specifically refers to the replacement of C–X with C–H.

Reply: We thank the reviewer for this valuable comment. The target transformation in "selective hydrodehalogenation of organohalides" is the replacement of C–X bonds with C–H bonds to form hydrogenated products. Within this definition, any reaction pathway that consumes the reactive species (such as electrons and active hydrogen species) but fails to yield the target C–H product constitutes a loss of selectivity. Specifically, the formation of dimeric and polymeric products is undesirable because (i) it may produce a dimer or oligomer with residual halogen atoms (incomplete dehalogenation), and (ii) even when fully dehalogenated, the coupling or high-molecular-weight products reduce the yield of the desired C–H product. For clarity, we have revised the relevant sentence as:

> "However, both pathways are often plagued by limited kinetics and poor product selectivity, as the high-energy intermediates readily undergo undesirable side reactions such as polymerization, coupling, or over-reduction, all of which divert the reaction flux away from the target C–H product." (Page 3, Lines 40-43)

(7) Scheme 1 was not cited in the manuscript.

Reply: We are sorry for this mistrake. During the revision, **Scheme 1** has now been cited in the manuscript as suggested.

> "The uncharged, radical-based nature of H• renders its reactivity fundamentally mismatched with the polar C–X bond, leading to inefficient direct hydrogenation and preferential dimerization into H_2 (**Scheme 1a**)." (Page 3, Lines 45-47)

> "The hydride ion ($H^{\delta-}$), with its inherent negative charge and potent nucleophilicity, is ideally suited for a direct, concerted attack on the electrophilic carbon ($C^{\delta+}$) of the polarized C–X bond (**Scheme 1b**)." (Page 4, Lines 55-57)

(8) Line 79: This paragraph reads like a conclusion section. It should be revised to instead present the study's hypothesis, key methodology, and research logic more clearly.

Reply: Thank you for this valuable suggestion. Revisions have been made to **Line 79** to remove concluding content and clarify the research hypothesis and experimental methods as follows.

"Guided by this mechanistic insight, we propose that mechanochemically activated ZVI with surface ($Si^{\delta+}$–$O^{\delta-}$) can in situ generate silicon-hydride (Si–$H^{\delta-}$) species and thus realize an interfacial hydride transfer for highly efficient hydrodehalogenation. To test this hypothesis, we construct these surface-confined Lewis acid-base pairs directly on the ZVI scaffold via a trace-water-assisted mechanochemical process ($SiH^{\delta-}$-ZVI), where ZVI generates H_2 through aqueous corrosion, and silicate pairs induce heterolytic H_2 cleavage to produce reactive silicon-hydride (Si–$H^{\delta-}$) species. A combination of *in situ* spectroscopic characterization and theoretical modelling is employed to elucidate the complete cycle of hydride formation and regeneration. The hydrogenation activity of $SiH^{\delta-}$-ZVI is evaluated through batch tests against diverse organohalide substrates. To further demonstrate the versatility of this hydride transfer platform, we investigate its application in regioselective deuteration for deuterated acetic acid synthesis and evaluate its practical scalability through continuous-flow column tests using authentic contaminated groundwater." (Pages 5-6, Lines 84-95)

(9) Line 162: The manuscript should clarify why florfenicol was selected as the model compound. Specifically, was its selection based on environmental relevance, structural features, or a combination of both? Especially given that the broad applicability of the material was tested by common chlorinated hydrocarbons in groundwater.

Reply: We appreciate the reviewer for this thoughtful question. Florfenicol (FF) was selected as the model compound based on a combination of environmental relevance and structural representativeness, as detailed below:

1. **Environmental relevance.** FF is a widely used veterinary antibiotic, frequently detected in aquaculture wastewater, surface water, and groundwater worldwide. Its environmental persistence and role in promoting antibiotic resistance (e.g., *floR*, *fexA* genes) make it a pollutant of great practical concern (*Environ. Sci. Technol.* **2024**, 58 (43), 19501-19513; *Environ. Sci. Technol.* **2018**, 52 (17), 9972-9982; *Environ. Res.* **2024**, 244, 117934).

2. **Structural representativeness.** FF contains both C–Cl and C–F bonds with distinctly different bond dissociation energies. This structural feature allows us to evaluate the stepwise hydrodehalogenation

capability of our $SiH^{\delta-}$-ZVI and to demonstrate the regioselectivity of the hydride transfer pathway within a single molecule.

3. **Complementary to broad applicability tests.** The subsequent experiments using common chlorinated hydrocarbons (TCE, PCE, CF, etc.) serve a different purpose for validating the substrate scope of $SiH^{\delta-}$-ZVI. Together, FF (as a structurally complex, environmentally relevant probe) and the chlorinated hydrocarbons (as representative groundwater contaminants) form a complementary evaluation system covering both mechanistic and practical studies.

   During the revision, we supplemented the corresponding discussion as:

   "Widely utilized as a veterinary antibiotic, florfenicol (FF) is commonly detected in natural waters. Owing to its notable environmental persistence and the coexistence of C–Cl and C–F bonds with distinct bond energies, FF was selected as a structurally representative target pollutant to assess the hydrodehalogenation performance of $SiH^{\delta-}$-ZVI." (Page 9, Lines 164-167)

(10) Line 196: The KIE values larger than one support the involvement of H_2O and, subsequently, surface hydride species in the dechlorination/defluorination reactions. However, why do these values also suggest that hydrogen transfer is the rate-limiting step?

Reply: Thank you for this critical question. The underlying principle is that the C–D bond has a lower zero-point energy than the C–H bond, resulting in a higher activation energy for the deuterated species. A KIE value greater than unity, typically > 1.5, is considered as evidence that proton transfer is involved in the rate-determining step (or, at least, in one of the steps affecting the reaction rate) (Biochim. Biophys. Acta-Bioenerg. 2000, 1458, 6–27; Nat. Commun. **2019**, 10, 5074).

For accuracy, we have revised the discussion:

"The KIE values for all three dehalogenation steps exceeded 1.5 (**Fig. 2d, and Supplementary Fig. 19, Table 3**), consistent with the involvement of hydrogen transfer from the catalyst surface in the rate-determining step (or, at least, in one of the steps affecting the reaction rate).[29,30]" (Page 12, Line 207-210)

(11) Contradictory statements need to be fixed: Line 169 states that "The enhanced activity was most pronounced during the hydrodechlorination stages", corresponding to a 12-fold increase. However, Line 185 reports that the defluorination rate constants increased by 20-fold. The authors should clarify this apparent inconsistency.

Reply: Thank you for pointing out this inconsistency. We have carefully revised the manuscript to eliminate the discrepancy as follows:

1. **Origin of the contradiction.** The original sentence "The enhanced activity was most pronounced during the hydrodechlorination stages" (**Line 169**) referred to qualitative observation of the overall degradation profile, while the statement that the defluorination rate constant increased by "20-fold" (**Line 185**) was misleading. Si-ZVI and pristine ZVI displayed undetectable defluorination performance under identical conditions, so computing a fold enhancement relative to a baseline of zero activity is mathematically invalid and misleading.

2. **Corrections made.** To solve this issue, we have made two revisions: (i) delete the sentence "The enhanced activity was most pronounced during the hydrodechlorination stages" from **Line 169**; (ii) revised **Line 185** to report the measured rate constant directly, without calculating a fold enhancement to zero activity as follows:

   "$SiH^{\delta-}$-ZVI achieved a measurable surface area-normalized defluorination rate constant ($k_{3,SA}$) of 0.002 ($L \cdot d^{-1} \cdot m^{-2}$), whereas no defluorination was observed for Si-ZVI or ZVI under identical conditions (**Supplementary Table 2**)." (Page 11, Lines 190-192)

(12) Line 171, the values of "1.7 and 5 times greater" do not match the data presented in Figure 2c.

Reply: We thank the reviewer for noticing the discrepancy between the values in Line 171 and those originally shown in **Fig. 2c**. We apologize for the confusion. The values "1.7 and 5 times greater" refer to the enhancement factors of the surface area-normalized rate constants ($k_{1,SA}$ and $k_{2,SA}$). We have revised Fig. 2c to display the promotion factors of surface normalized k_{obs}.

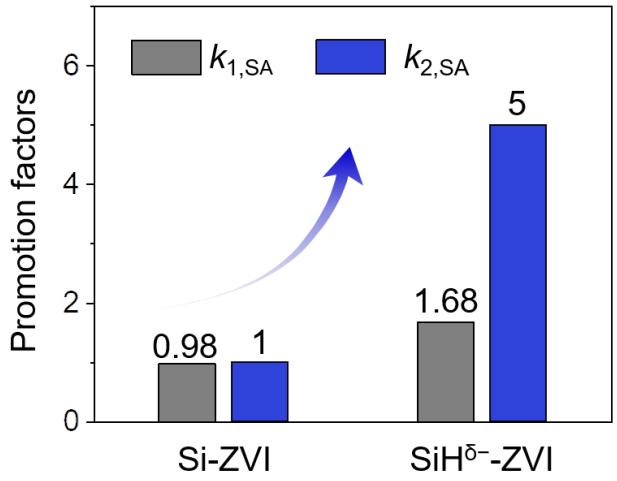


Figure 2c. Promotion factors of surface-normalized k_{obs} for the conversion of FF ($k_{1,SA}$) and dFF ($k_{2,SA}$) by SiH$^{\delta-}$-ZVI and Si-ZVI relative to pristine ZVI. (Page 11, Lines 181-183)

(13) Fig. 2f: The figure legends, including labels such as H_2O, m/z values, and explanatory notes such as Si-H, should be updated to accurately reflect the synthesis and reactions of SiD-ZVI with D_2O.

Reply: Thanks for the suggestion. We have revised the legends of **Fig. 2f** to accurately reflect the experimental conditions and synthesis of SiD$^{\delta-}$-ZVI as follows. The labels (H_2O, *m/z*, Si–H$^{\delta-}$, etc.) have been updated accordingly.

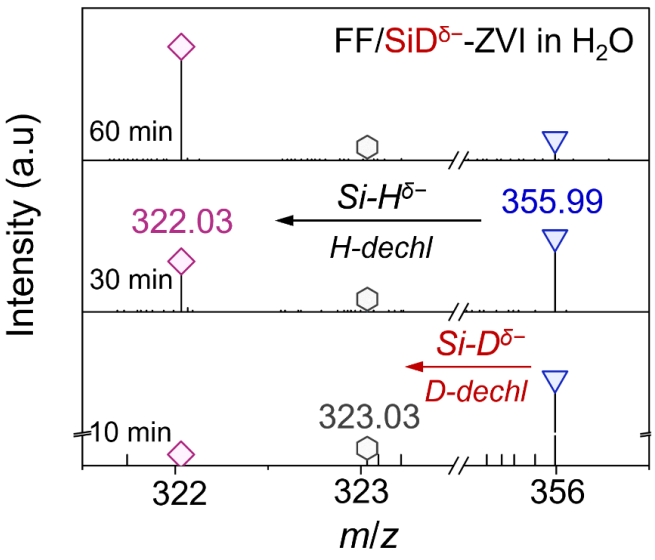


Figure 2f. Time-resolved mass spectra of FF degradation by SiD$^{\delta-}$-ZVI in H_2O. The SiD$^{\delta-}$-ZVI was prepared under the same ball milling conditions as SiH$^{\delta-}$-ZVI except that H_2O was replaced by D_2O." (Page 11, Lines 184-186)

(14) Line 320: The authors demonstrate the broad applicability of the method using several common chlorinated contaminants. However, many of these contaminants can be readily degraded by other materials, including modified ZVI systems. If the novelty of this study lies in developing a new material for decontamination, the authors should provide a clearer rationale for why such a material is needed for these contaminants and demonstrate its advantages over previously reported materials.

Reply: We sincerely thank the reviewer for this insightful comment, which helps us better articulate the novelty and significance of our work.

This study does not focus on the development of another high-performance ZVI material for contaminant removal, but establishes a fundamentally new dehalogenation pathway via direct interfacial hydride transfer ($H^{\delta-}$) on the ZVI surface, which is different from the traditional stepwise electron/hydrogen transfer pathways. Accordingly, in this study, our research primarily focuses on the mechanochemical construction of surface hydrides, interfacial hydrogen transfer, and the regeneration mechanism, rather than claiming overall superiority over all existing ZVI systems.

In response to the reviewer's suggesttion, we have added a comparative analysis of dechlorination kinetics between our $SiH^{\delta-}$-ZVI and the most widely used S-ZVI that was prepared under identical conditions (*J. Hazard. Mater.* **2023**, 446, 130730; *Environ. Sci. Technol.* **2017**, 51, 12653-12662). We note that we have not compared our material with all other reported ZVI systems, because the dehalogenation performance of such materials can vary significantly with changes in preparation methods and parameters. Instead, we have provided a rigorous comparison with a well-defined S-ZVI synthesized under identical mechanochemical ball-milling conditions as follows.

> "Compared with a widely used S-ZVI prepared under identical mechanochemical ball-milling conditions, $SiH^{\delta-}$–ZVI demonstrates superior dechlorination kinetics for the tested chlorinated hydrocarbons (**Supplementary Table 7**)." (Page 18, lines 350-353)

Supplementary Table 7. Comparative degradation rates of chlorinated hydrocarbons by $SiH^{\delta-}$-ZVI and S-ZVI. (SI, Page 62, Lines 561-562)

Chlorinated hydrocarbons	$SiH^{\delta-}$-ZVI		S-ZVI		Data Source
	k_M ($h^{-1}\cdot g^{-1}\cdot L$)	k_{SA} ($L\cdot h^{-1}\cdot m^{-2}$)	k_M ($h^{-1}\cdot g^{-1}\cdot L$)	k_{SA} ($L\cdot h^{-1}\cdot m^{-2}$)	

PCE	0.003	0.002	0.001	0.0009	
TCE	0.01	0.0087	0.021	0.014	
trans-DCE	0.09	0.078	0.004	0.003	Wu[40]/Gu[23]
cis-DCE	0.07	0.061	0.0005	0.0004	
VC	0.025	0.021	0.0004	0.0004	

(15) Line 369: The authors should clarify why deuterated acetic acid is considered a valuable product. Does the reported 98% purity meet the requirements for its intended application? In addition, the manuscript should explain the advantages of the $SiH^{\delta-}$-ZVI approach compared with current industrial production methods. As currently presented, the valorization discussion appears somewhat disconnected from the main text. Alternatively, the authors should more clearly emphasize the importance and technical need for the selective replacement of C–X bonds with C–H bonds. Otherwise, the valorization part reads more as an attempt to broaden the impact of the current work, rather than as a component to advance scientific questions.

Reply: We sincerely thank the reviewer for this valuable comment. We agree that the original valorization discussion was presented in a way that appeared disconnected from the main scientific narrative. We have substantially revised it to address this concern.

1. **Why is deuterated acetic acid (AA-d_4) a valuable product, and whether 98% purity meet the requirements?**

Deuterated compounds are indispensable in pharmaceutical research, analytical chemistry, and material science, with a market price exceeding $5 per gram (e.g., Aladdin, ≥99.9% D, $39.43/g; Macklin, 99.5% D, $17.77/g; J&K/CIL, 98% D, $5.24/g). Specifically, AA-d_4 serves two critical roles:

(i) As a high-value chemical itself: AA-d_4 is a key internal standard for mass spectrometry (MS) in metabolomics, pharmacokinetics, and environmental analysis.

(ii) As a versatile synthetic intermediate and deuterium source: AA-d_4 can be further converted into other deuterated reagents, such as deuterated acetic anhydride and deuterated ester. These compounds are widely used to introduce trideuteromethyl (CD_3) and deuterated carbonyl groups into organic

molecules, enabling kinetic isotope effect (KIE) studies, mechanistic investigations, and the synthesis of deuterium-labeled pharmaceuticals and agrochemicals.

The reported >98% purity, determined by NMR (**Fig. 4g**), is sufficient for analytical and synthetic applications. For analytical internal standards, a purity of >98% is not recommended for strict quantification, but it can be used for semi-quantitative or general comparative experiments. For synthetic intermediates, this purity level is generally acceptable for subsequent transformations, because the final products undergo subsequent purification steps.

2. **Advantages of the $SiH^{\delta-}$–ZVI approach compared with current industrial production methods.**

Current industrial production of AA-d_4 relies on multi-step routes under harsh conditions, involving expensive deuterated agents (like acetone-d_6), noble metal catalysts, and harsh high-temperature reaction conditions(*Adv. Synth. Catal.* **2016**, 358, 3277-3282; *Nat. Synth.* **2022**, 1, 824–830; *Org. Lett.* **2004**, 6, 1485−1487; *Nat. Commun.* **2025**, 16, 10365). Our method offers several distinct advantages:

(i) Mild and safe conditions: operates at ambient temperature and pressure, using D_2O as the sole deuterium source, eliminating the need for high-pressure D_2 gas.

(ii) Simplified separation: the heterogeneous catalyst ($SiH^{\delta-}$-ZVI) enables straightforward recovery of AA-d_4 from TCAA (**Figs. 4e-g**), directly converting a common pollutant into a valuable product without byproduct separation.

(iii) Atomic economy: the $SiH^{\delta-}$-ZVI species regenerates through water dissociation, minimizing waste and potentially enabling a circular process.

3. **Connection to the main science contribution.**

We have revised the manuscript to frame this valorization not as an add-on application, but as a direct demonstration of the regioselectivity and synthetic utility of the interfacial hydride transfer mechanism. The selective deuteration of TCAA to AA-d_4 exemplifies the regioselectivity of the hydride transfer pathway, in which a polar C–X bond is cleaved, and deuterium is incorporated at a specific position. The application, therefore, advances the central scientific question of how to harness interfacial hydride transfer for selective chemical transformations.

During the revision, we revised the corresponding discussion.

“Demonstrating its synthetic utility, we applied $SiH^{\delta-}$-ZVI to the selective hydrodechlorination and regioselective deuteration of trichloroacetic acid (TCAA), a common chlorinated pollutant. $SiH^{\delta-}$-ZVI achieved complete conversion to deuterated acetic acid (AA-d_4) with 93.4% selectivity, yielding 2.37 g of >98% pure product after simple separation. As a versatile deuterium source and synthetic intermediate, AA-d_4 can be further converted into deuterated acetyl chloride, acetic anhydride, and esters for downstream applications. This result directly validates the ability of the interfacial hydride transfer pathway to achieve precise C–X bond functionalization under mild conditions.” (Page 22, Lines 403-410).

Reviewer 2: The authors report a mechanochemically activated zero-valent iron (ZVI) platform that, in the presence of trace water and silicate-derived interfacial Lewis acid-base pairs, generates nucleophilic Si–$H^{\delta-}$ species to drive highly efficient and regioselective dehalogenation. This platform demonstrates rapid kinetics, water-mediated regeneration of active sites, and practical application in continuous-flow treatment of real contaminated groundwater. It seems interesting and attractive, but there remain several issues with the writing format and mechanistic explanation. Publication should be considered after a minor revision. Specific comments are listed below.

1. Scheme 1. "Interfacial hydride transfer" in the caption should use lowercase "I" (i.e., "interfacial") for consistency with "conventional hydrogen atom transfer".

Reply: We thank the reviewer for noticing this. In the caption of **Scheme 1**, we have changed "Interfacial hydride transfer" to "interfacial hydride transfer".

> "**Scheme 1.** Schematic comparison of hydrodehalogenation processes via **a.** conventional hydrogen atom transfer and **b.** interfacial hydride transfer." (Page 4, Lines 52-53)

2. In Figure 1b. "Rention Time" on the x-axis should be corrected to "Retention Time".

Reply: We are sorry for this typo. In **Fig. 1b**, the x-axis label has been corrected from "Rention Time" to "Retention Time".

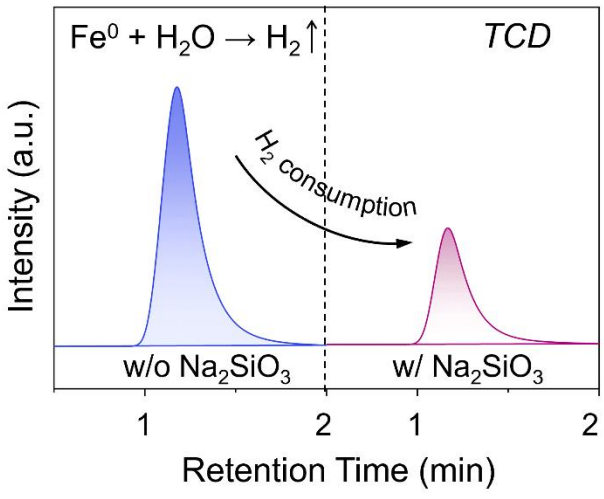


Figure 1b. GC-TCD profiles of H_2 signals obtained from the mechanochemical agitation of ZVI and trace

H_2O in the absence and presence of Na_2SiO_3. (Page 8, Lines 123-125)

3. In Figure 2g. The label "Transtimmittance" contains a spelling error. Please correct this to "Transmittance". And the y-axis label incorrectly places the unit outside the parentheses. Please standardize this notation to match journal conventions.

Reply: We thank the reviewer for pointing out the spelling error and the incorrect placement of the unit. In **Fig. 2g**, the y-axis label has been corrected from "Transtimmittance" to "Transmittance", and the unit has been placed inside parentheses as "Transmittance (%)".

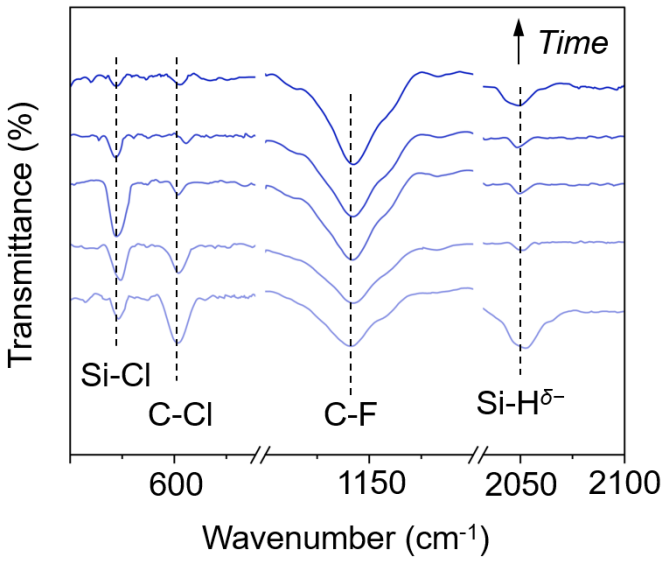


Figure 2g. *In-situ* FTIR spectra of FF degradation by $SiH^{\delta-}$-ZVI in H_2O (10 min, 20 min, 40 min, 2 h, and 5 h) in the range of 550-2100 cm^{-1}. (Page 11, Lines 186-188)

4. In Figure 3. The legend "Raman shift (cm^{-1})" in figures d and e contains a clear written error. Please correct this to "Raman shit (cm^{-1}); The reaction coordinate on the x-axis of figure f isn't fully visible, it may be obscured by the graph below. The label "regeneation" in the mechanism cycle contains a spelling error, please correct this to "regeneration".

Reply: We thank the reviewer for pointing out these errors. In **Fig. 3**, we have corrected "Raman shit" to "Raman shift", made the x-axis label "Reaction coordinate" fully visible, and changed "regeneation" to "regeneration" as follows.

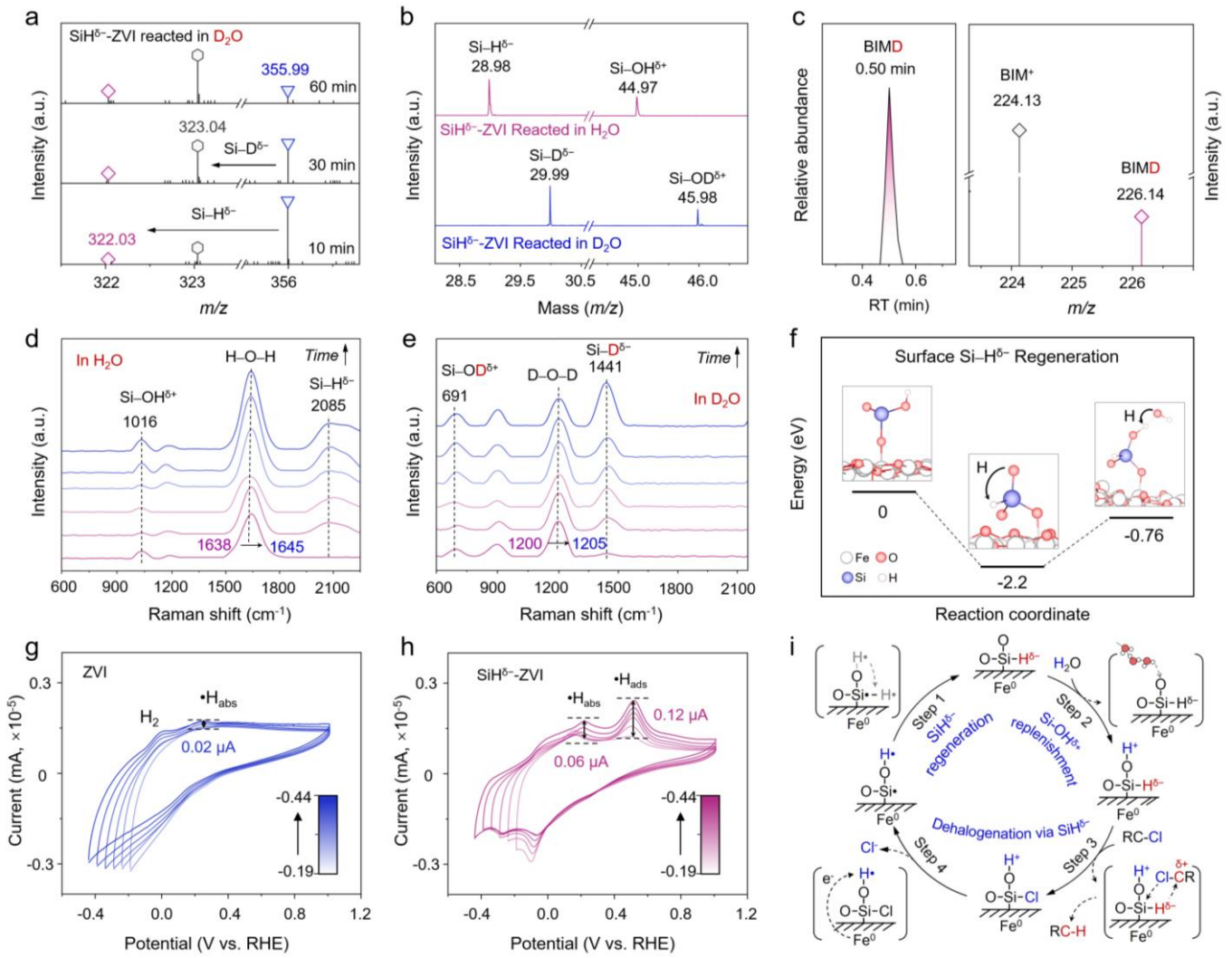


Figure 3. Surface hydride regeneration. a. Time-resolved mass spectra of FF conversion over $SiH^{\delta-}$-ZVI in D_2O. **b.** High-resolution TOF-SIMS spectra of $SiH^{\delta-}$-ZVI reacted in H_2O and D_2O solutions. **c.** The identification of hydrogenated products of BIM^+ with the reacted $SiH^{\delta-}$-$ZVI_{(D_2O\text{-}FF)}$ through electrospray ionization mass spectrometry (ESI-MS), and the associated MS spectrum of BIMD. In-situ Raman spectra of **d.** the reacted $SiH^{\delta-}$-$ZVI_{(H_2O\text{-}FF)}$ with H_2O and **e.** the reacted $SiH^{\delta-}$-$ZVI_{(D_2O\text{-}FF)}$ in D_2O. Cyclic voltammetry curves of **f.** ZVI and **g.** $SiH^{\delta-}$-ZVI in an Ar-saturated Na_2SO_4 solution from -0.19 to -0.44 V vs. RHE. **h.** Energy profiles of $Si–H^{\delta-}$ regeneration on $SiH^{\delta-}$-ZVI via $Si–OH^{\delta+}$ and water dissociation. **i.** Schematic diagram of dehalogenation via $Si–H^{\delta-}$ and its regeneration on $SiH^{\delta-}$-ZVI. (Pages 15-16, Lines 280-288)

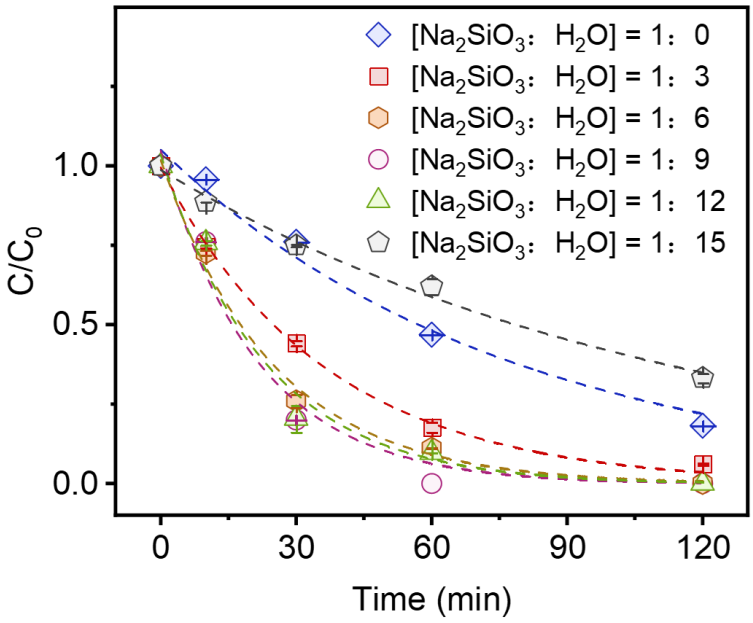
5. The manuscript refers to “trace water”, and the actual amount used is 69 μL. Could the authors clarify how this water dosage was determined, and why this specific volume was selected as the optimal condition for surface hydride formation and dehalogenation performance?

Reply: We appreciate the reviewer's attention to the synthesis details. The volume of water (69 µL) was determined through systematic optimization in the preliminary experiments.

During the synthesis of $SiH^{\delta-}$-ZVI, the volume of deionized water (as the hydrogen source) was varied to achieve Na_2SiO_3:H_2O molar ratios from 1:0 to 1:15, corresponding to water volumes of 0, 23, 46, 69, 92, and 115 µL. The resulting materials were evaluated by their performance in FF degradation (**added as Supplementary Fig. 1**).

The degradation activity increased with water volume up to 69 µL (1:6 molar ratio), beyond which further addition of water led to a decline in performance. This trend indicates an optimal level of surface hydration; insufficient water limits hydride formation, while excess water likely causes over-corrosion of the ZVI core. The sample prepared with 69 µL of water exhibited the highest activity and was therefore selected as the optimal condition. We have clarified this rationale in the revised Supplementary manuscript as follows.

> "The volume of deionized water added as H source was systematically optimized. Samples prepared with 0, 23, 46, 69, 92 and 115 µL water, corresponding to the Na_2SiO_3: H_2O molar ratio ranging from 1:0 to 1:15, were evaluated based on their performance in FF degradation. The $SiH^{\delta-}$-ZVI synthesized with 69 µL exhibited the highest FF degradation activity; therefore, this volume was selected as optimal for subsequent material characterization and experiments." (SI, Page 19, Lines 369-373)



Supplementary Figure 1. Kinetics of FF degradation fitted to a first-order kinetic model by $SiH^{\delta-}$-ZVI under different volumes of water. Reaction conditions: ZVI dosage = 10 $g \cdot L^{-1}$, FF = 20 ppm, 50 mM HEPES, pH 7, anoxic, T = 25°C. (SI, Page 19, Lines 363-367)

6. It would be better to include some introduction and discussion on recently reported modifications of nZVI and ZVI materials, such as sulfidation and latter engineering, which also show good performance on dehalogenation. This may help readers recognize specific application scenarios of different materials.

Reply: We appreciate the valuable suggestion. We have compared the dehalogenation performance of $SiH^{\delta-}$-ZVI with widely used S-nZVI, and corresponding discussions have been added as follows:

> "Notably, the rate constants for defluorination (i.e., $k_{3,SA}$) by $SiH^{\delta-}$-ZVI were more than 1.92 higher than that of the most widely used nanoscale S-ZVI (S-nZVI)." (Page 11, Lines 193-195)

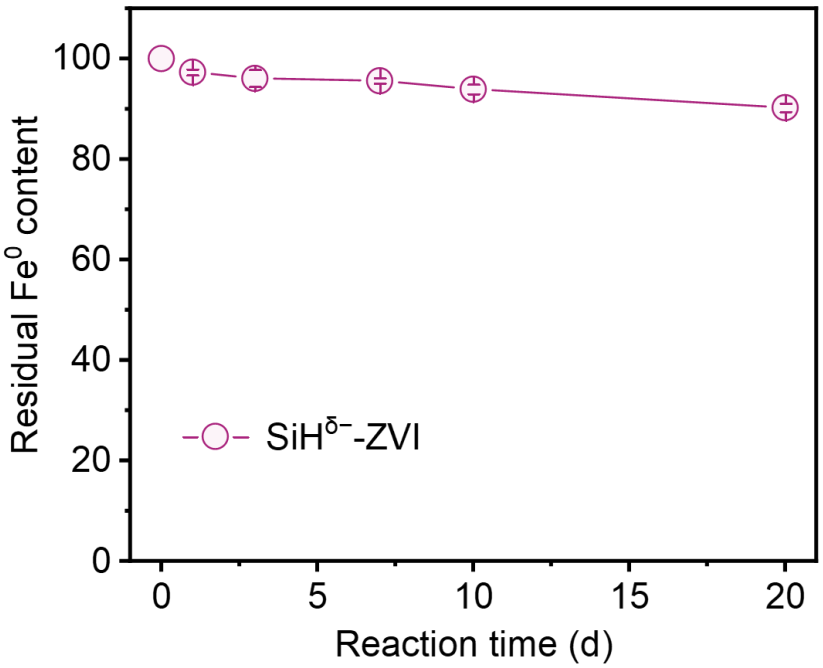
7. As ZVI provides electrons, a passivation layer of iron oxides/hydroxides will inevitably form. How does this insulating layer affect the generation of $Si–H^{\delta-}$ over time? Can the $SiH^{\delta-}$-ZVI and other reference materials be regenerated after the ZVI core is completely oxidized?

Reply: We appreciate the insightful question. The regeneration of $Si–H^{\delta-}$ depends on two key factors: (i) the sustained electron transfer capacity of the ZVI core, and (ii) the retention of surface silicon sites.

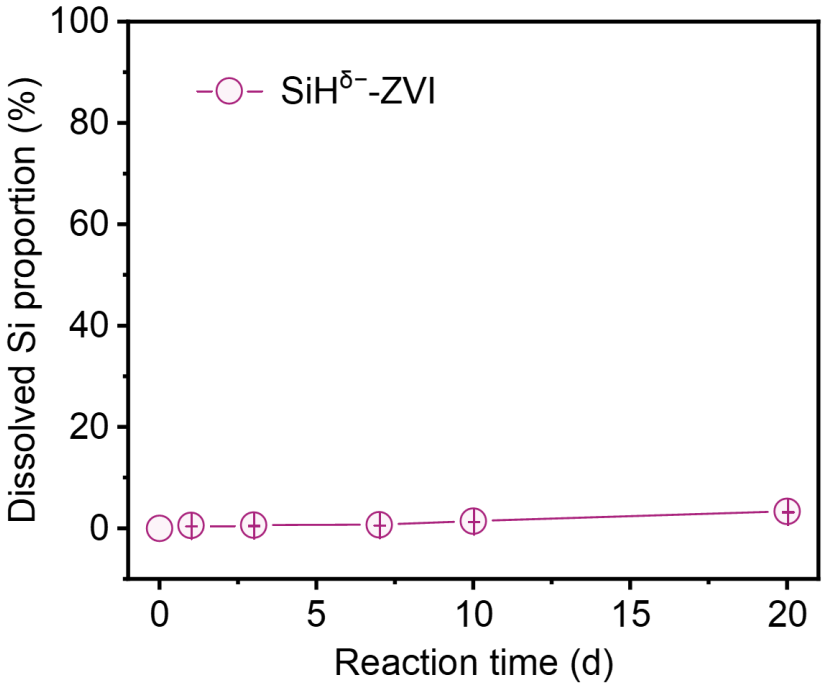
To address the concern regarding possible deactivation by the passivation layer, we monitored the residual Fe^0 content and silicon leaching during the FF degradation process. The results revealed that after 20 days of reaction, the Fe^0 content of $SiH^{\delta-}$-ZVI decreased by less than 10% (**added as Supplementary Fig. 28**), while cumulative silicon leaching accounted for less than 4% of the initial silicon content (**added as Supplementary Fig. 29**). These results confirm that the iron oxide/hydroxide layer formed during reactions does not significantly impede electron transfer from the Fe^0 core to the surface over this timescale, and the surface silicon sites remain sufficiently stable to anchor the cyclic regeneration of Si–$H^{\delta-}$ active sites (**Fig. 3**).

Nevertheless, we acknowledge that once the ZVI core is completely oxidized and loses its electron transfer capacity, Si–$H^{\delta-}$ species can no longer be regenerated. This represents an inherent limitation of the material's lifetime, which is common to all ZVI-based systems. We have included this discussion in the revised manuscript to provide a balanced assessment of the material's long-term applicability.

> "After 20 days of FF degradation, the Fe^0 content of $SiH^{\delta-}$-ZVI decreases by less than 10% (**Supplementary Fig. 28**), and silicon leaching accounts for less than 4% of the initial silicon content (**Supplementary Fig. 29**). The residual Fe^0 content of the ZVI can sustain continuous electron transfer for in-situ proton reduction, and the retained surface silicon sites provide stable anchoring centers for the cyclic generation of Si–$H^{\delta-}$ active species, thereby enabling steady Si–$H^{\delta-}$ regeneration during long-term hydrodehalogenation." (Page 18, Lines 337-342)



Supplementary Figure 28. Variation of residual Fe^0 content in $SiH^{\delta-}$-ZVI during FF degradation. Reaction conditions: Fe^0 = 10 g·L^{-1}, FF = 20 ppm, 50 mM HEPES, pH 7, anoxic, T = 25 °C. (SI, Page 46, Lines 493-496)



Supplementary Figure 29. Cumulative Si leaching percentage relative to total initial Si content of $SiH^{\delta-}$-ZVI during FF degradation. Reaction conditions: Fe^0 = 10 g·L^{-1}, FF = 20 ppm, 50 mM HEPES, pH 7, anoxic, T = 25 °C. (SI, Page 47, Lines 497-500)

8. Line 234–240. The authors state that the persistence of the Si–$H^{\delta-}$ signal in the in situ FTIR spectra indicates regeneration rather than stoichiometric consumption of the active hydride species. Could the authors provide quantitative evidence that the FTIR signal intensity truly reflects the concentration of catalytically active Si–$H^{\delta-}$ sites?

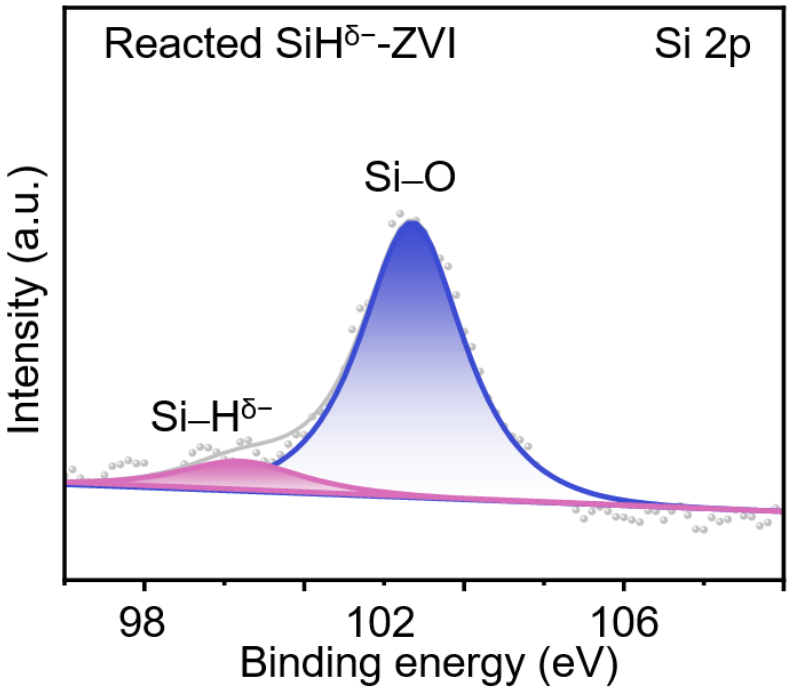
Reply: We thank the reviewer for this important comment. We agree that establishing a strict quantitative relationship between FTIR peak intensity and surface Si–$H^{\delta-}$ concentration is challenging. To best address this concern, we provide the following lines of evidence:

1. **The non-monotonic trend itself is diagnostic.**

   We first conducted peak area integration for the characteristic stretching peak of Si–$H^{\delta-}$ at ~2052 cm^{-1} based on the time-resolved in-situ FTIR spectra (**Fig. 2g**). Even without assuming perfect linearity between peak area and concentration, the observed decrease followed by a sustained increase (**added as Supplementary Fig. 23**) constitutes a qualitative signature that cannot be explained by a simple stoichiometric consumption model (which would predict a monotonic decrease). The only physically plausible interpretation for this trend is that the Si–$H^{\delta-}$ species undergo *in situ* regeneration during the reaction. This peak area analysis thus provides strong semi-quantitative support for the proposed regeneration cycle.

2. **The FTIR trend is consistent with independent characterization methods.**

   The initial consumption of Si–$H^{\delta-}$ observed in FTIR coincides with the rapid degradation of FF (**Fig. 2b**), while the subsequent recovery of the Si–$H^{\delta-}$ signal matches the slower later-stage kinetics. Furthermore, Si 2p XPS analysis of the post-reaction $SiH^{\delta-}$-ZVI confirmed the continued presence of the Si–$H^{\delta-}$ species at a concentration comparable to the as-prepared material (**Supplementary Fig. S24, Table S5**). TOF-SIMS analysis (**Fig. 3b**) also independently verified the retention of the Si–$H^{\delta-}$ signal after reaction. The convergence of these three techniques (FTIR, XPS, TOF-SIMS) on the same conclusion—that Si–$H^{\delta-}$ persists and regenerates—provides confidence in the reliability of the FTIR observation.



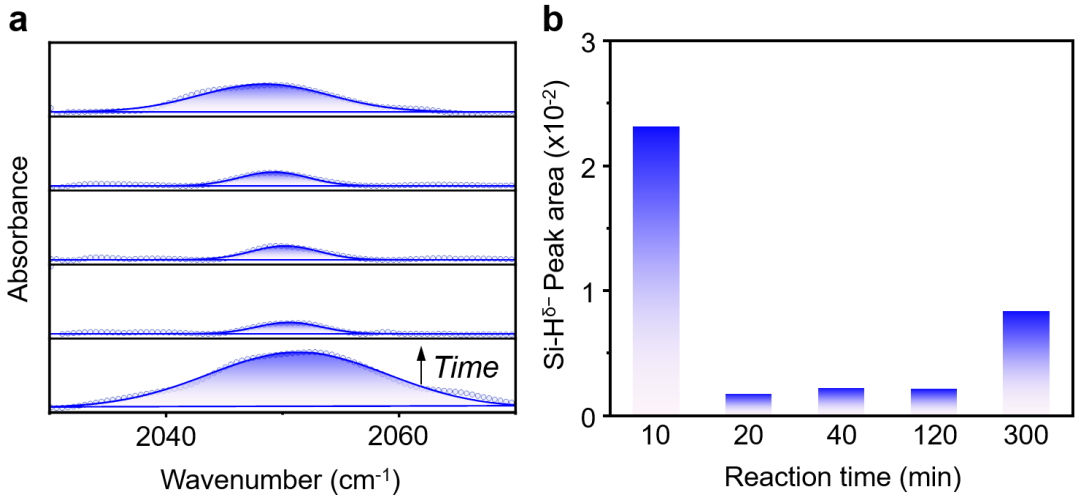
Supplementary Figure 24. Si 2p XPS spectra of reacted SiH$^{\delta-}$-ZVI after SiH$^{\delta-}$-ZVI reaction with FF in H_2O for 1 h (reacted SiH$^{\delta-}$-ZVI$_{(H2O\text{-}FF)}$).

Supplementary Table 5. Relative contents of Si–H$^{\delta-}$and Si-O species in the Si 2p XPS spectra of fresh SiH$^{\delta-}$-ZVI and that after 1 h reaction with FF.

Materials	Si–H$^{\delta-}$ (99.2 eV)	Si–O (101.4 eV)
SiH$^{\delta-}$-ZVI	16.3	83.7
Reacted SiH$^{\delta-}$-ZVI	15.3	84.7

We have revised the manuscript text accordingly:

"As the reaction progressed, a clear spectral evolution was observed with the continuous decay of the C–Cl peak and the initial decrease and subsequent increase of the Si–H$^{\delta-}$ peak (**Supplementary Fig. 23**). This non-monotonic trend, consistent with initial consumption and subsequent regeneration of the active hydride species, is independently corroborated by post-reaction XPS analyses" (Page 14, Lines 242-246)



Supplementary Figure 23. a. Time-dependent integrated peak area and **b.** temporal variation of absolute peak area of the Si–$H^{\delta-}$ characteristic band at 2052 cm^{-1} derived from *in-situ* FTIR spectra during FF degradation by $SiH^{\delta-}$-ZVI (**Fig. 2g**). (SI, Page 41, Lines 476-479).

9. The proposed mechanism in figure 3i involves the formation of surface-bound Si–Cl/F intermediates during dehalogenation. Could the accumulation of these cleaved halide species on the catalyst surface poison or block the active sites, for example by competitive adsorption or irreversible site occupation?

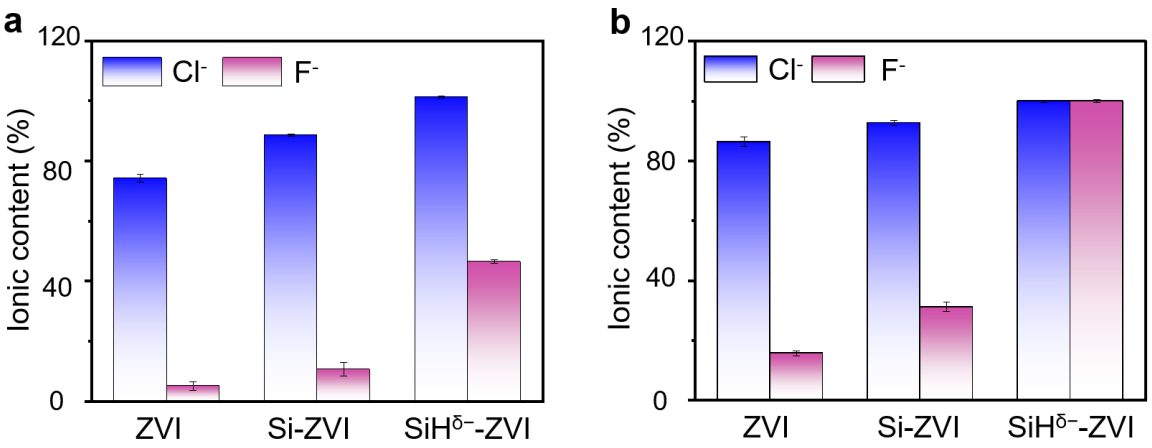
Reply: We thank the reviewer for this valuable comment. The formed surface Si–Cl/F intermediates are transient species that do not permanently block the active sites according to the following evidences.

1. **In-situ spectroscopic evidence.**

   As shown in **Fig. 2g**, the in-situ FTIR spectra reveal the emergence and growth of a Si–Cl stretching vibration at 575 cm^{-1} during FF degradation. However, this signal does not accumulate irreversibly; instead, it represents a transient intermediate formed during the SN_2-like attack of surface hydride on the C–Cl bond, followed by rapid release of free Cl^- into solution.

2. **Chlorine mass balance analysis.**

   We performed a quantitative chlorine mass balance by measuring aqueous Cl^- concentrations via ion chromatography (**Supplementary Fig. 17**). The results show that after complete FF degradation (**Supplementary Fig. 17a**), over 99% of the chlorine originally present in the substrate was released as free Cl^- in solution, with negligible residual Si–Cl species on the catalyst surface.



Supplementary Figure 17. Cl^- and F^- released during FF degradation by the ZVIs: a. after 20 days; b. after 40 days of reaction. Reaction conditions: Fe^0 = 10 g·L^{-1}, FF = 20 ppm, 50 mM HEPES, pH 7, anoxic, T = 25 °C.

3. **Complete dehalogenation efficiency.**

As shown in **Supplementary Fig. 17b**, $SiH^{\delta-}$-ZVI achieves 100% dechlorination and defluorination of FF within 40 days. This complete conversion would be impossible if active sites were progressively poisoned by accumulating halide species.

Taken together, these results confirm that the Si–Cl/F intermediates are short-lived species that undergo facile hydrolysis to release free halide ions, rather than irreversibly blocking the active sites. We have added a brief discussion of the chlorine mass balance to the revised manuscript.

"$SiH^{\delta-}$-ZVI achieves 100% dechlorination and defluorination efficiency for FF degradation after 40 days of reaction. The complete dehalogenation confirms that the cleaved halide species do not accumulate on the material surface, and thus cause no active site poisoning or blocking." (SI, Page 35, Lines 450-453)

10. For large-scale sustainable remediation, how does the cost of synthesizing Si-ZVI compare with traditional ZVI material or other widely used iron-based remediation materials?

Reply: We thank the reviewer for raising this important practical question regarding large-scale sustainable remediation. We have compared the cost of our material with that of currently reported commercial nZVI products (Toda Kogyo Corp., Japan; NANO IRON s.r.o., Czech Republic; Macklin Biochemical Co., Ltd, China), as well as several widely used and cost-quoted ZVI-based materials, including S-nZVI (*Nat. Sustain*. **2024**, 7, 1264–1272.), TG^{me}-mZVI (*Angew. Chem. Int. Ed.* **2025**, 64, e202415051.),

and strained-mZVI (Adv. Funct. Mater. 2022, 32, 2200498). The detailed results are presented in **Supplementary Tables S12 and S13** as follows.

"Notably, the cost of $SiH^{\delta-}$-ZVI was only about $1899.2 per ton, which is lower than that of both commercial and laboratory-prepared nanoscale ZVI as well as other reported microscale ZVIs (**Supplementary Tables 12-13**)" (Page 21, Lines 400-402).

Supplementary Table 12. The manufacturing cost of $SiH^{\delta-}$-ZVI and other ZVI (per ton). (SI, Page 67, Lines 579-580)

Material	Feed stock ($/ton)			Manufacturing expenses ($/ton)	Other cost ($/ton)[a]	Total cost ($/ton)
$SiH^{\delta-}$-ZVI	mZVI	Na_2SiO_3	H_2O	1000	500	1899.2
	386.67	10.7	1.83			
S-nZVI[22]	$FeCl_3$	$NaBH_4$	$Na_2S_2O_4$	84.09	/	17412.51
	417.2	16688.7	222.52			
TG^{me} -mZVI[8]	mZVI		TG	1000	500	1907.31
	386.67		20.64			
Strained-mZVI[41]	mZVI		B_2O_3	1000	500	1956.67
	386.67		70			

a: Other costs include transportation and storage costs.

Supplementary Table 13. The price of commercial nZVI (per ton). [41] (SI, Page 68, Lines 581-582)

nZVI	Product name	Manufacturer	Total cost ($/ton)

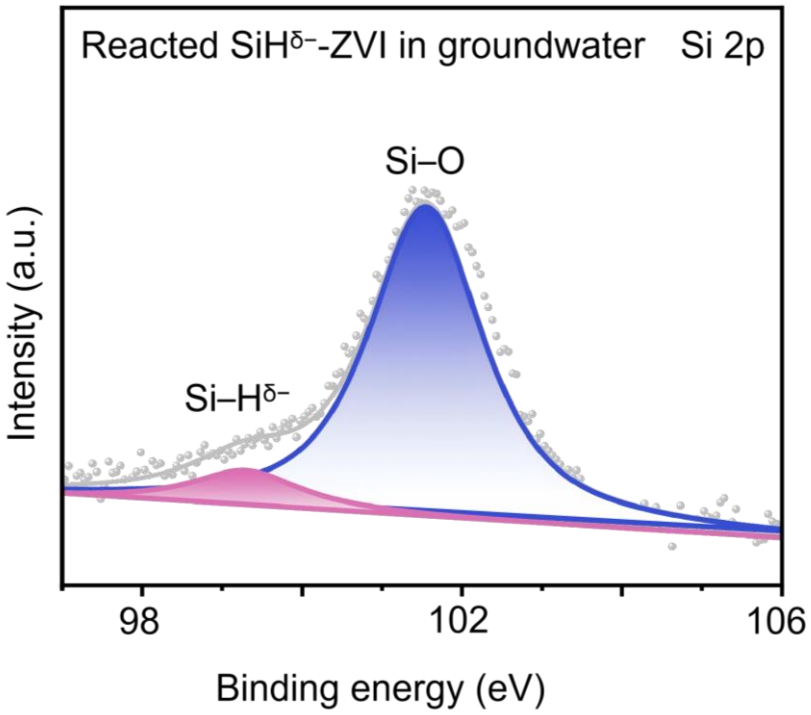
nZVI	Reactive nanoscale iron particles	Toda Kogyo Corp., Japan	80000
nZVI	NANO FER	NANO IRON s.r.o., Czech Republic	140000
nZVI	Nanoscale iron	Macklin Biochemical Co., Ltd, China	1500000

11. How do groundwater matrices (humic acid, cations, carbonates) influence Si–$H^{\delta-}$ stability?

Reply: We appreciate the reviewer for the valuable comment. We have carried out batch experiments using actual groundwater from industrial sites in Taizhou, which contains natural organic matter and bicarbonate, to evaluate the Si–$H^{\delta-}$ stability and passivation resistance of $SiH^{\delta-}$-ZVI under real remediation conditions. Detailed water quality parameters about organic matter and bicarbonate, as well as cations, have been added in **Supplementary Table 10.** Relevant results and discussion have been incorporated into the revised manuscript as follows. Additionally, we performed detailed characterization on $SiH^{\delta-}$-ZVI materials collected after both batch groundwater experiments. The results are summarized below and confirm the stability of the active sites.

> "To assess practical applicability, the dechlorination efficacy of $SiH^{\delta-}$-ZVI was evaluated using real groundwater from an industrially contaminated site (Taizhou, Zhejiang, China), which contained a complex matrix of organic matter, bicarbonate, and cations, as well as co-contaminants including chlorinated solvents, Cr(VI), and As (**Supplementary Table 10**)." (Page 20-21, Lines 378-381)

> "Si 2p XPS of $SiH^{\delta-}$-ZVI collected after batch experiment confirmed that the Si–$H^{\delta-}$ structure was well retained (**Supplementary Fig. 36**)." (Page 21, Lines 387-389)



Supplementary Figure 36. Si 2p XPS spectra of reacted $SiH^{\delta-}$-ZVI in real groundwater. (SI, Page 54, Lines 533-534)

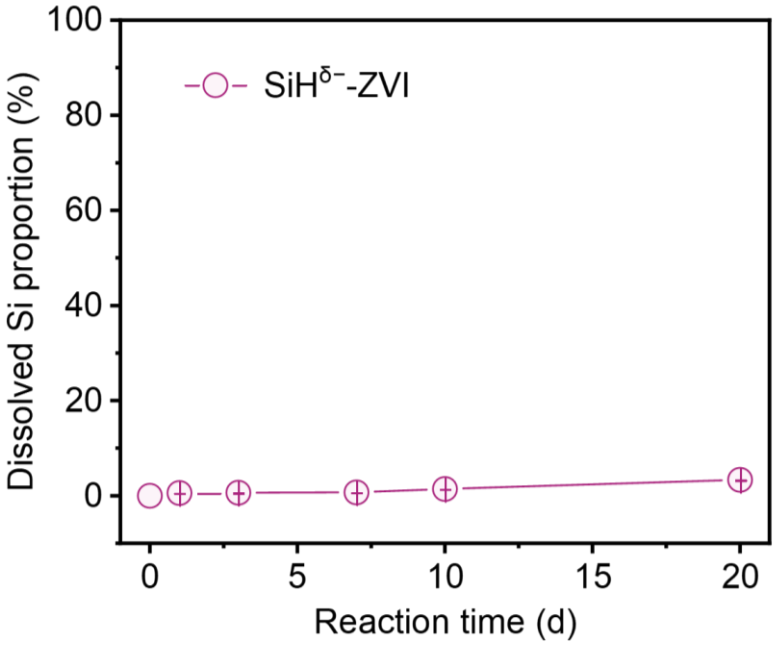
Supplementary Table 10. Compositional and physicochemical parameters of real groundwater collected from an industrial site in Taizhou. (SI, Page 65, Lines 572-573)

Parameters	Concentration ($ug \cdot L^{-1}$)
Ca^{2+}	58440
Mg^{2+}	143670
Na^{+}	777435
TOC	567400
CO_3^{2-}	681000
TCE	115
Hg	7.03

Pb	50.67
Cr(VI)	150
As	98

12. Are there any dissolved silicon species leaching into the solution during the dehalogenation process? What is the chemical stability of the Si shell?

Reply: We systematically evaluated the chemical stability of the silicate shell on $SiH^{\delta-}$-ZVI by conducting time-dependent leaching tests. Both fresh pristine material and samples collected at different reaction stages were analyzed via inductively coupled plasma mass spectrometry (ICP-MS) to quantify dissolved silicon in the aqueous phase. In the 40 mL reaction system loaded with 0.4 g of $SiH^{\delta-}$-ZVI, the concentration of leached silicon reached 1.65 mg/L after 20 days of continuous reaction. The cumulative leached silicon accounted for only 3.36% of the total silicon initially contained in the material.

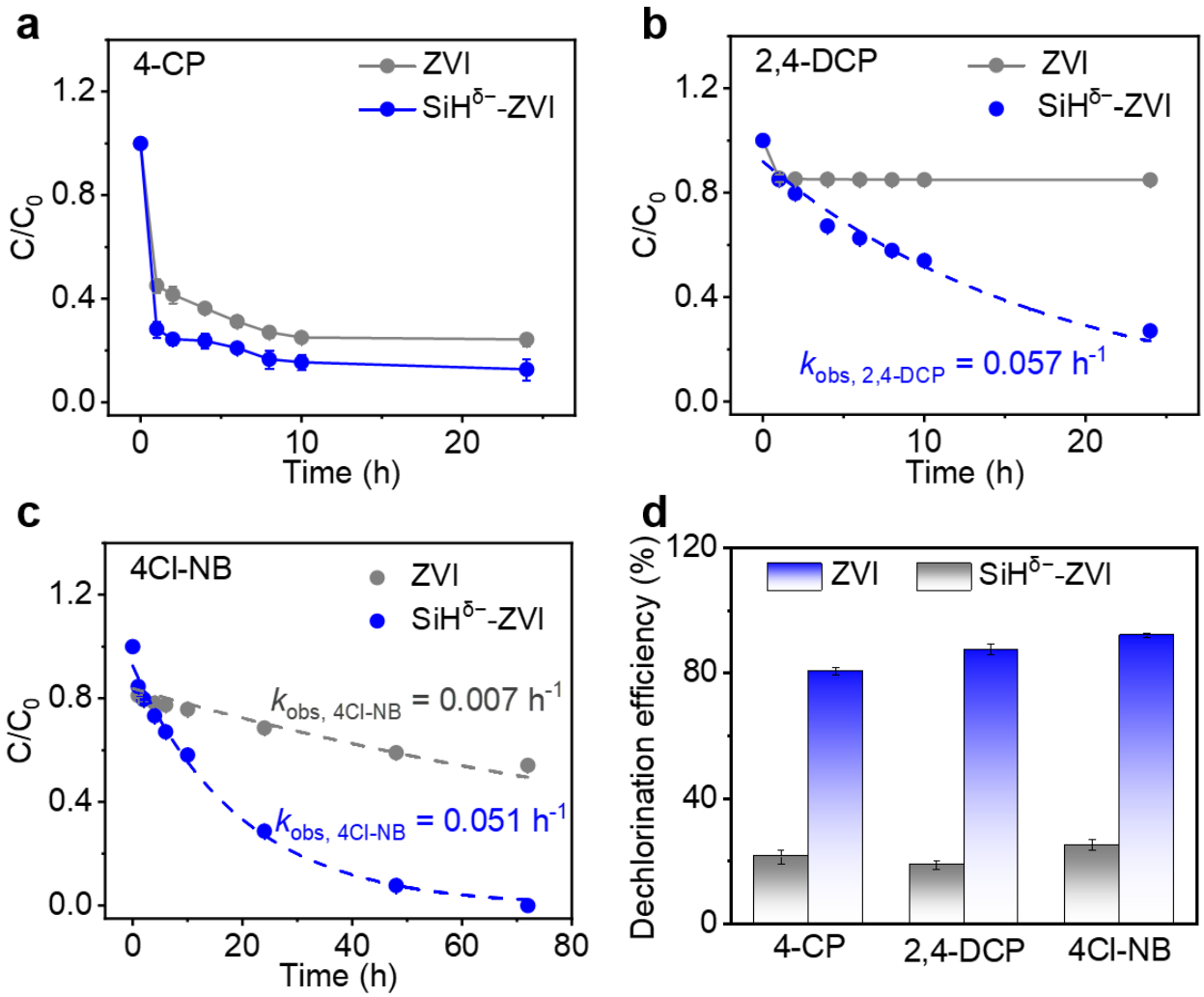


Supplementary Figure 28. Cumulative Si leaching percentage relative to total initial Si content of $SiH^{\delta-}$-ZVI during FF degradation. Reaction conditions: Fe^0 = 10 g·L^{-1}, FF = 20 ppm, 50 mM HEPES, pH 7, anoxic, T = 25 °C. (SI, Page 46, Lines 494-496)

"**Analysis of Silicon Leaching.** To evaluate the chemical stability of the silicate shell, the concentration of dissolved silicon in the reaction solution was measured at 1, 3, 7, 10, and 20 d. At each time point, an aqueous sample was collected, filtered through a 0.22 μm PES membrane, and the filtrate was digested with nitric acid at 250 °C for 1 h. After cooling, the solution was diluted to 10 mL with ultrapure water and analyzed by ICP-MS (Agilent 7900) under optimized conditions (RF power = 1550 W, carrier Ar flow = 1.05 $L \cdot min^{-1}$, auxiliary gas flow = 0.9 $L \cdot min^{-1}$, sampling depth = 8 mm).[12] Silicon concentrations were quantified using calibration curves from standard solutions (0-1000 $\mu g \cdot L^{-1}$). The cumulative silicon leaching ratio was calculated based on the total silicon content in the as-prepared $SiH^{\delta-}$-ZVI." (SI, Page 11, Lines 198-207)

13. While the authors demonstrate high reactivity of $Si–H^{\delta-}$ toward aliphatic C–X bonds (e.g., TCE), it remains unclear whether this interfacial hydride transfer is equally effective for aromatic compounds or PFAS, which have significantly higher bond dissociation energies. Could the authors elaborate on the scope and limitations of their system?

Reply: We appreciate the reviewer's comment. Indeed, the substrate scope, especially toward stronger C–X bonds, deserves a clearer experimental delineation. To address this, we expanded our test panel to include several chlorinated aromatics: 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP), and 4-chloronitrobenzene (4Cl-NB). The results are now **added as Supplementary Figure 31**. Under identical conditions, $SiH^{\delta-}$-ZVI achieved dechlorination efficiencies of 80%-92% within three days for all three aromatic substrates, whereas pristine ZVI showed less than 26% conversion, with mass balance analysis indicating that most of the apparent loss from solution was due to adsorption rather than reductive transformation. These results demonstrate that the interfacial hydride transfer pathway is effective for aromatic C–Cl bonds, despite their higher bond dissociation energies compared to aliphatic C–Cl bonds. The success can be attributed to the concerted two-electron nature of hydride transfer, which bypasses the high-energy radical intermediates that are particularly problematic for aromatic substrates.

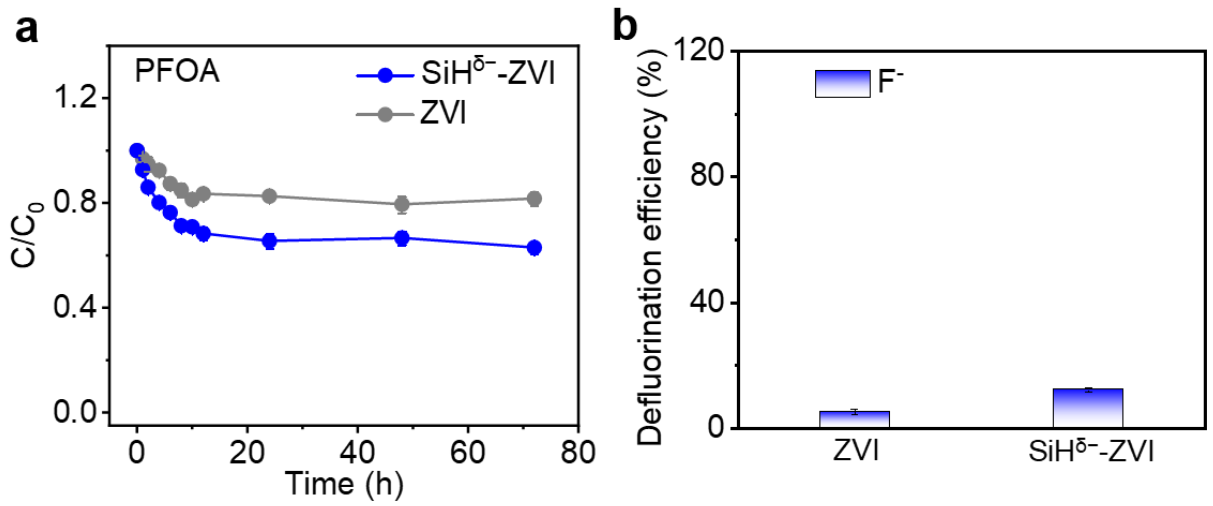


Supplementary Figure 31. Degradation kinetics of other chlorinated carbons, including **a.** 2,4-dichlorophenol (2,4-DCP), **b.** 4-chlorophenol (4-CP), and **c.** 4-chloronitrobenzene (4Cl-NB), by ZVI and SiHδ−-ZVI fitted to a first-order kinetic model. **d.** Percent dechlorination of these chlorinated carbons by ZVI and SiH$^{\delta-}$-ZVI. Reaction conditions: [Fe] = 10 g·L-1, [aromatic pollutants] = 100 μM, 50 mM HEPES buffer, pH 7.0, anoxic conditions, T = 25 °C.. Reaction conditions: [Fe] = 10 g·L^{-1}, [aromatic pollutants] = 100 μM, 50 mM HEPES buffer, pH 7.0, anoxic conditions, T = 25 °C. (SI, Page 49, Lines 507-513)

"The superior dechlorination performance of SiH$^{\delta-}$-ZVI was demonstrated across a spectrum of common chlorinated contaminants, including trichloroethene (TCE), tetrachloroethene (PCE), chloroform (CF), and their daughter products *cis*-/*trans*-1,2-dichloroethene (DCE) and vinyl chloride (VC), as well as 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP), and 4-chloronitrobenzene (4Cl-NB). The material exhibited significantly enhanced reaction rates, with observed pseudo-first-order

rate constants for chlorinated hydrocarbons 2 to 50 times greater than those of pristine ZVI" (Page 18, Lines 344-350)

Regarding PFAS, $SiH^{\delta-}$-ZVI only exhibited marginal removal of perfluorooctanoic acid (PFOA), with a rate constant slightly higher than that of pristine ZVI under anaerobic conditions (**added as Supplementary Fig. 32**). The limited efficacy can be attributed to two factors: (i) perfluorinated C–F bonds possess exceptionally high bond dissociation energies (~485 kJ mol^{-1}) and pronounced kinetic inertness, and (ii) the long, rigid perfluorinated carbon backbone and the strong electron-withdrawing effect of the fluorine atoms create a sterically hindered and electronically deactivated environment. We have added the following statement to the revised manuscript to explicitly acknowledge this limitation:



Supplementary Fig. 32. **a.** Degradation of PFOA by $SiH^{\delta-}$-ZVI. **b.** Corresponding defluorination efficiency. Reaction conditions: Fe^0 = 10 g·L^{-1}, PFOA = 20 ppm, 50 mM HEPES, pH 7, anoxic, T = 25 °C. (SI, Page 50, Lines 514-517)

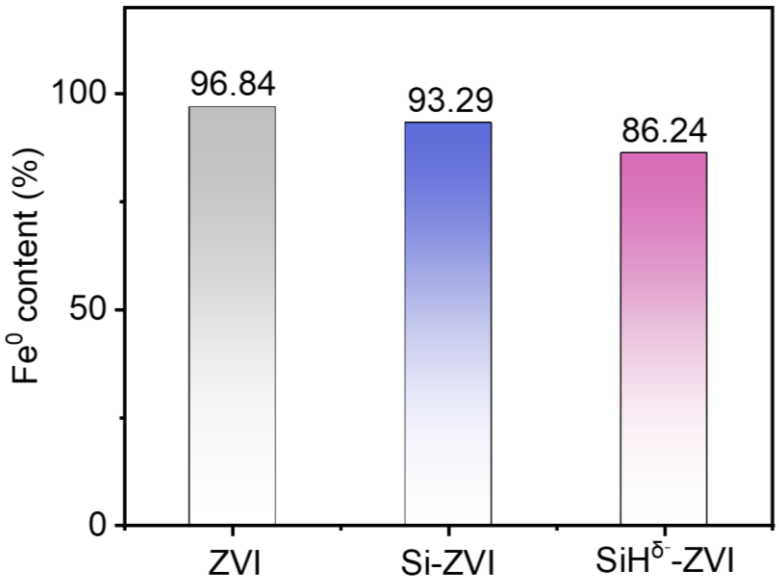
"Nevertheless, the reactivity of $SiH^{\delta-}$-ZVI toward perfluorinated compounds is limited due to the extreme stability of perfluorinated C–F bonds and the steric hindrance of the perfluorinated chains (**Supplementary Fig. 32**). Developing strategies to extend the interfacial hydride transfer mechanism to PFAS represents an important direction for future catalyst design." (Page 18-19, Lines 353-357)

Reviewer 3: This manuscript titled "Interfacial hydride transfer for sustainable dehalogenation with water" presents a novel mechanochemically activated zero-valent iron (ZVI) material that enables interfacial hydride transfer for efficient hydrodehalogenation of organic halides. The authors provide compelling spectroscopic, electrochemical, and computational evidence supporting the formation of SiHδ− species and their catalytic role. The work is innovative, well-executed, and has significant implications for both environmental remediation and green chemical synthesis. Therefore, I recommend publication after all the following issues were well addressed. The comments are listed below.

1.The manuscript describes the synthesis of $SiH^{\delta-}$-ZVI by ball-milling iron powder with sodium silicate and trace water. However, it is unclear whether the metallic Fe^0 content of ZVI changes significantly after $SiH^{\delta-}$ modification (e.g., due to Fe^0 corrosion). Please provide quantitative analysis of the Fe^0 content of $SiH^{\delta-}$-ZVI and ZVI to support the stability of the electron reservoir.

Reply: Thanks a lot for the comment. We have added quantitative Fe^0 content data of pristine ZVI, Si-ZVI, and $SiH^{\delta-}$-ZVI in the Supporting Information (**added as Supplementary Fig. 9**). The Fe^0 contents are 96.84%, 93.29%, and 86.24%, respectively. Despite a decrease in Fe^0 content caused by trace water during ball milling, both $SiH^{\delta-}$-ZVI maintains Fe^0 content of ZVI and Si-ZVI about 86-92%. Such a minor variation indicates negligible Fe^0 corrosion after modification, demonstrating the stable electron reservoir of $SiH^{\delta-}$-ZVI. The relevant results have been incorporated into the revised manuscript.

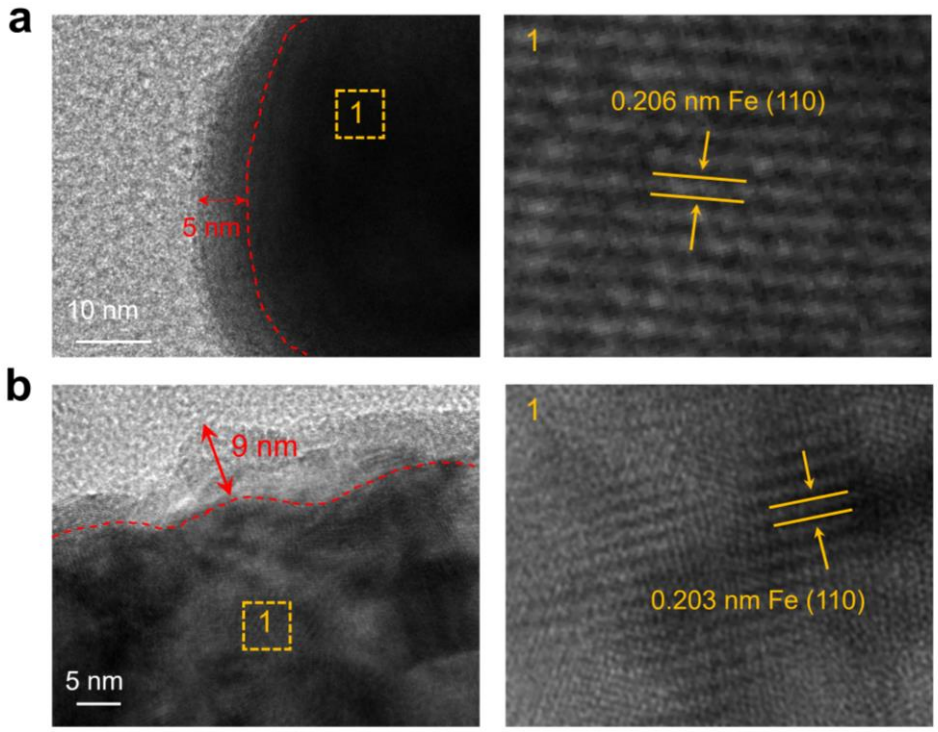
> "The Fe^0 content of the prepared ZVI particles was quantified via acid digestion. Briefly, around 10 mg of ZVI sample was dispersed in a mixed solution containing 1 mL of 37% concentrated HCl and 4 mL of deoxygenated ultrapure water, following a previously reported protocol.[6] The mixture was shaken continuously for 12 h to ensure sufficient reaction. The produced hydrogen gas was subsequently analyzed using a GC-TCD system (Agilent 9790). The final Fe^0 content was calculated based on the stoichiometric relationship defined in **Eq. S1**.
>
> $$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow \qquad (S1)$$" (SI, Page 8, Lines 149-155)



Supplementary Figure 9. Fe^0 content of ZVI, Si-ZVI, and $SiH^{\delta-}$-ZVI. (SI, Page 28, Lines 410-411)

2. The core-shell structure is mentioned based on HRTEM/HAADF-STEM images (SI Figs. S7-S8). Could the authors provide statistical data or representative measurements of the oxide shell thickness of $SiH^{\delta-}$-ZVI and ZVI? A discussion on how ball milling with silicate and water affects shell morphology of ZVI would strengthen the material characterization.

Reply: Thanks a lot for the valuable suggestion. We have statistically analyzed the oxide shell thickness based on HRTEM images, as shown in **Supplementary Fig. 8**. The surface silicon hydride modification well preserves the core-shell structure of ZVI, with the oxide shell thickness decreasing from approximately 9 nm for pristine ZVI to 5 nm for $SiH^{\delta-}$-ZVI (**Supplementary Fig. 8)**. The corresponding results and discussion have been supplemented in the revised manuscript as follows.



Supplementary Figure 8. HRTEM images of **a.** $SiH^{\delta-}$-ZVI, **b.** ZVI. Insets show higher-magnification views of the regions marked "1" (yellow boxes), with measured lattice spacing corresponding to the Fe (110) crystal plane.

> "The surface silicon hydride modification well preserves the core-shell structure of ZVI, with the oxide shell thickness decreasing from approximately 9 nm for pristine ZVI to 5 nm for $SiH^{\delta-}$-ZVI." (SI, Page 26, Lines 404-406)

3. The authors propose that "the metallic Fe core acts as an electron reservoir, which is crucial for stabilizing the electron-rich surface hydride species." To strengthen this claim, a more direct assessment of the material's electron release capacity after $SiH^{\delta-}$ modification, especially compared to pristine ZVI would be valuable. Please consider adding a brief analysis, for example via Tafel analysis or electrochemical impedance spectroscopy (EIS) measurement to evaluate corrosion potential and charge transfer resistance. This would clarify how $SiH^{\delta-}$ modification influences the electron donation ability of the ZVI.

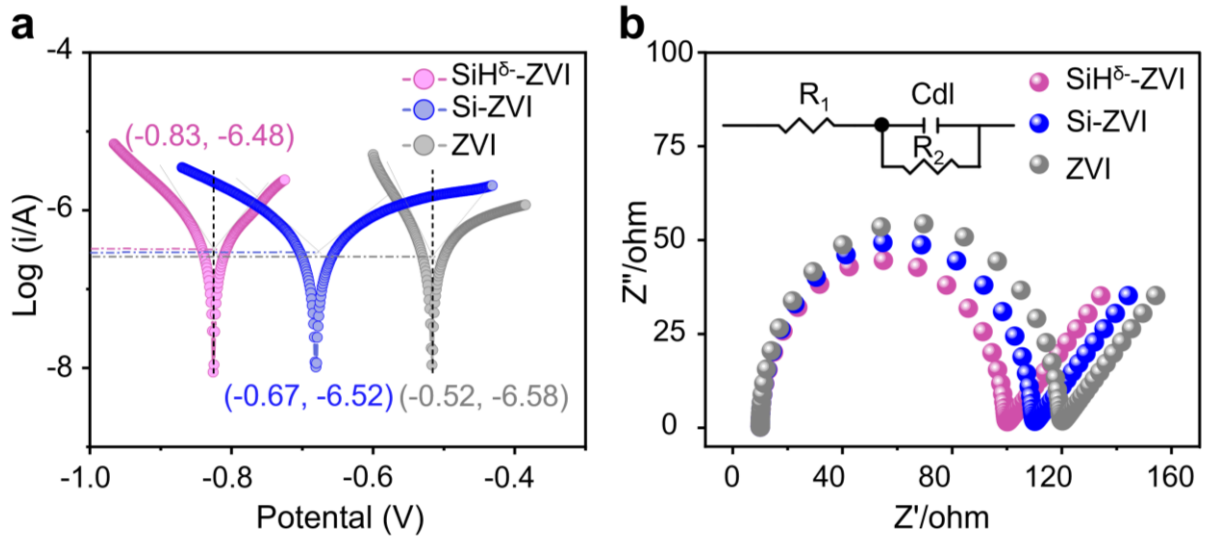
Reply: Thanks a lot for this kind suggestion. To assess the electron release capacity of the ZVIs, we have performed Tafel polarization and electrochemical impedance spectroscopy (EIS) measurements on pristine ZVI, Si-ZVI, and $SiH^{\delta-}$-ZVI. The results show that $SiH^{\delta-}$-ZVI exhibits a more negative corrosion potential and a lower charge transfer resistance, indicating enhanced electron transfer capability. These

data have been incorporated into the revised manuscript as follows.

"Electrochemical analysis, including Tafel curves, Electrochemical impedance spectroscopy (EIS), were performed using a CHI-760 Electrochemical Workstation (CHI Instruments, Chenhua, China, Shanghai) in a standard three-electrode system according previous studies.[4,5,7] A glassy carbon electrode was used as the working electrode, coated with a 0.4 mm thick iron powder layer, with an effective area of 1 mm^2.[8] Ag/AgCl served as the reference electrode, and a platinum (Pt) counter electrode. The electrolyte was 0.1 M sodium sulfate (Na_2SO_4). After recording the open circuit potential (OCP) for 1 hour, EIS measurements were performed at the OCP with a sinusoidal potential perturbation amplitude of 5 mV, over a frequency range of 100 kHz to 10 mHz.[9,10] Finally, Tafel curve tests were carried out at a scan rate of 0.01 V/s, with a potential range of -1.2 V to -0.5 V." (SI, Page 9, Lines 156-166)

"Electrochemical characterization was used to investigate the effect of $SiH^{\delta-}$ modification on the electron transfer properties of ZVI. Tafel polarization curve analysis shows that $SiH^{\delta-}$-ZVI had the lowest corrosion potentials (approximately -0.83 V vs. -0.63 V for Si-ZVI; -0.83 V vs. -0.52 V for ZVI) and higher corrosion currents (approximately 0.33 μA vs. 0.30μA for Si-ZVI; 0.33 μA vs. 0.26 μA for ZVI) compared with that of ZVI and Si-ZVI. Meanwhile, EIS showed that $SiH^{\delta-}$-ZVI had a lower charge transfer resistance (100 Ω) compared to Si-ZVI (110 Ω) and ZVI (120 Ω). These results collectively confirm that $SiH^{\delta-}$ modification could facilitate electron emission and interfacial transfer of ZVI." (SI, Page 29, Lines 418-425)

"Based on the Fe^0 content, along with electrochemical impedance and corrosion current measurements (**Supplementary Figs. 10-11**), we propose that this metallic Fe core acts as an electron reservoir, which is crucial for stabilizing the electron-rich surface hydride species." (Page 8, Lines 138-141).



Supplementary Figure 11. Electrochemical Characterization of $SiH^{\delta-}$-ZVI, Si-ZVI, and ZVI. **a.** Tafel polarization curves; **b.** Nyquist plots fitted to an equivalent circuit model comprised of electrolyte resistance (Rs), charge transfer and contact resistance (Rct) and a constant phase element (CPE). (SI, Page 29, Lines 412-416)

4. In situ FTIR (Fig. 2g) reveals a Si-Cl stretching vibration at 575 cm^{-1} that grows during the reaction, suggesting that chloride released from C–Cl bond cleavage is captured by surface silicon. While the authors show that $SiH^{\delta-}$-ZVI signals persist after reaction (SI Fig. S19), it is not clear whether accumulated Si-Cl species gradually deactivate the active sites over extended operation. It would be valuable to evaluate the chlorine mass balance (e.g., whether Cl^- is fully released into solution or partially accumulates on the catalyst surface). A short discussion on this point would enhance the practical relevance.

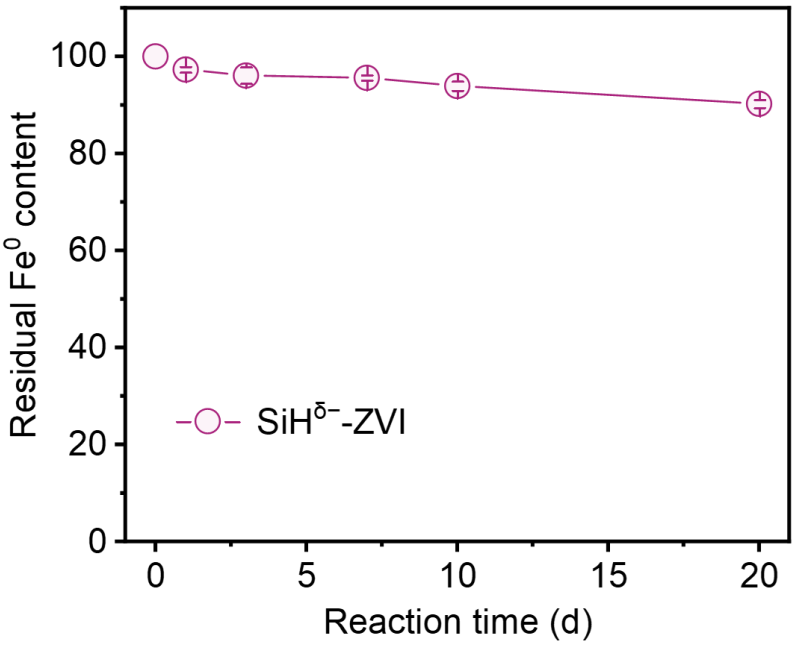
Reply: Thank you very much for this insightful comment. To address the concern regarding possible progressive deactivation caused by Si–Cl species, a chlorine mass balance analysis was performed by measuring the Cl^- concentration in the solution after reaction using ion chromatography (**Supplementary Fig. 17**). Therefore, the Si-Cl species observed by in situ FTIR (**Fig. 2g**) are transient intermediates rather than persistent deactivating species.

> "Ultimately, $SiH^{\delta-}$-ZVI achieved complete dechlorination and defluorination of FF within 40 days" (Page 11, Lines 197-198)

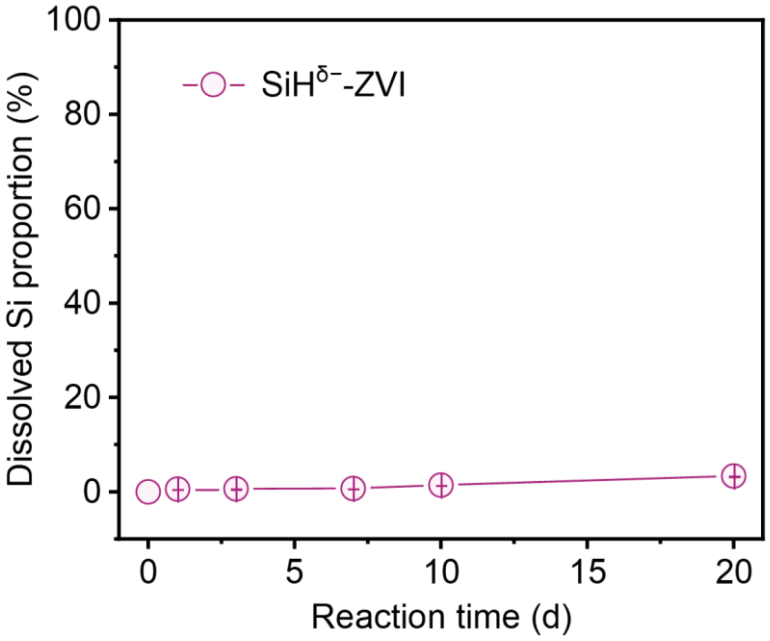
5.The proposed regeneration cycle relies on electron transfer from the Fe^0 core to regenerate $SiH^{\delta-}$-ZVI. Over extended reaction times, the Fe^0 content should gradually decrease. However, the manuscript does not provide any quantitative measurement of the residual Fe^0 content after long-term reaction (i.e., measurement of Fe^0 content after prolonged reaction). It would be valuable to determine the Fe^0 content in the post-reaction $SiH^{\delta-}$-ZVI and compare it with the fresh material. This would directly support the proposed "electron reservoir" role and help evaluate the material's long-term electron supply capacity.

Reply: We appreciate the insightful suggestion. The regeneration of $Si–H^{\delta-}$ depends on the sustained electron transfer capacity of the ZVI core. We monitored the variations of Fe content of $SiH^{\delta-}$-ZVI during the FF degradation process. The results revealed that the Fe content of $SiH^{\delta-}$-ZVI decreased by less than 10% after 20 days of reaction. These results confirm that the ZVI core maintains stable electron transfer capability for the continuous in-situ regeneration of $Si–H^{\delta-}$ active sites (**Fig. 3**). For clarity, corresponding discussions have been added as follows.

> "After 20 days of FF degradation, the Fe^0 content of $SiH^{\delta-}$-ZVI decreases by less than 10% (**Supplementary Fig. 28**), and silicon leaching accounts for less than 4% of the initial silicon content (**Supplementary Fig. 29**). The residual Fe^0 content of the ZVI can sustain continuous electron transfer for in-situ proton reduction, and the retained surface silicon sites provide stable anchoring centers for the cyclic generation of $Si–H^{\delta-}$ active species, thereby enabling steady $Si–H^{\delta-}$ regeneration during long-term hydrodehalogenation." (Page 18, Lines 337-342)



Supplementary Figure 28. Variation of residual Fe^0 content in $SiH^{\delta-}$-ZVI during FF degradation. Reaction conditions: Fe^0 = 10 g·L^{-1}, FF = 20 ppm, 50 mM HEPES, pH 7, anoxic, T = 25 °C. (SI, Page 46, Lines 493-496)



Supplementary Figure 29. Cumulative Si leaching percentage relative to total initial Si content of $SiH^{\delta-}$-ZVI during FF degradation. Reaction conditions: Fe^0 = 10 g·L^{-1}, FF = 20 ppm, 50 mM HEPES, pH 7, anoxic, T = 25 °C. (SI, Page 47, Lines 498-501)

6.Minor editorial corrections. Page 10: “forlenicol” should be corrected to “florfenicol”. Reference 12: “keteneous catalysis” should be “heterogeneous catalysis”. Figure 2a inset: the unit of kobs is missing; please add (e.g., min^{-1} or h^{-1}). There is a spelling error on page 3 in the Introduction section: “undesira0bl” should be corrected (e.g., to “undesirable”).

Reply: We sincerely apologize for these typographical errors. We have corrected them and have undertaken a thorough revision of the entire manuscript to ensure the highest standard of presentation.

7. You report that the electron selectivity (ε_e) of $SiH^{\delta-}$-ZVI in real groundwater is increased by 185 times compared to pristine ZVI (Fig. 4c), whereas in a buffer system the increase is only 6.8 times (SI Fig. 24f). What is the main reason for this large difference?

Reply: Thank you very much for this insightful comment. The large difference in electron efficiency (ε_e) enhancement between the buffer system (6.8-fold) and real groundwater (185-fold) arises from the combined impacts of the water matrix on hydrogen evolution reaction (HER) and dehalogenation.

For $SiH^{\delta-}$-ZVI, ε_e increases from 4.03% in buffer to 7.43% in groundwater. This is because groundwater constituents (e.g., NOM, bicarbonate) suppress the hydrogen evolution reaction (HER) more effectively than dehalogenation on the Si-modified surface, likely by stabilizing the surface hydride layer and limiting proton reduction at non-selective sites.

For pristine ZVI, ε_e drops dramatically from 0.59% in buffer to 0.04% in groundwater. Groundwater components promote surface passivation (e.g., iron carbonate/hydroxide precipitates), which preferentially inhibits the electron transfer required for dehalogenation over the competing HER pathway.

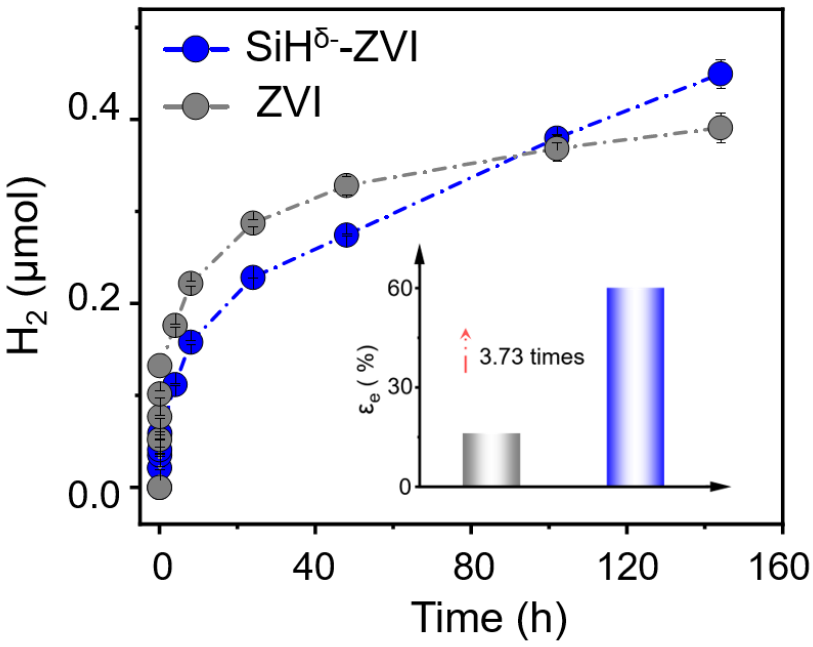
Therefore, the enhancement ratio ($\varepsilon_{e,SiH^{\delta-}\text{-ZVI}}/\varepsilon_{e,ZVI}$) is calculated as 4.03/0.59 ≈ 6.8 in buffer, but becomes 7.43/0.04 ≈ 185 in groundwater. This dramatic increase in groundwater is arisen from the combined effect, where groundwater moderately improves the ε_e of $SiH^{\delta-}$-ZVI by preferentially suppressing HER, while simultaneously and drastically lowering the ε_e of pristine ZVI by preferentially suppressing dehalogenation. These observations are fully consistent with the role of $Si–H^{\delta-}$ as a dehalogenation-selective site.

8. In the TCE dechlorination by ZVIs, you demonstrate the enhancement of electron efficiency (ε_e) by a factor of 6.8–185 and attribute it to the suppression of hydrogen evolution by $SiH^{\delta-}$-ZVI. However, for

florfenicol (FF), the most important model pollutant in the manuscript, you only report the rate enhancement factors without presenting the electron efficiency or the extent of hydrogen evolution inhibition. Could you please provide the electron efficiency of $SiH^{\delta-}$-ZVI in the FF system, and the enhancement factor relative to the control groups (Si-ZVI or ZVI)?

Reply: We thank the reviewer for this insightful comment. For the florfenicol (FF) system, we have now added the electron efficiency (ε_e) of $SiH^{\delta-}$-ZVI The results show that $SiH^{\delta-}$-ZVI achieves an ε_e of 60.1%, which is 3.73-fold higher than that of pristine ZVI (16.1%) (**added as Supplementary Fig. 18**), with corresponding descriptions added as follows.

> "Given the negatively polarized nature of the surface hydride, the hydrogen evolution reaction (HER) is effectively suppressed during FF degradation by $SiH^{\delta-}$-ZVI, compared to ZVI. Specifically, the electron selectivity of $SiH^{\delta-}$-ZVI for FF degradation, quantified by electron efficiency (ε_e),[28] is about 4 times higher than that of ZVI (**Supplementary, Fig. 18**)." (Page 11, Lines 201-205)



Supplementary Figure 18. H_2 evolution during FF degradation by $SiH^{\delta-}$-ZVI and ZVI. Inset: Electron efficiency (ε_e) of the ZVIs toward FF degradation. (SI, Page 36, Lines 455-457)