Peer Review File

Title: Adjacent single-atom irons boosting molecular oxygen activation on MnO2

<b>REVIEWER COMMENTS</B>

Reviewer #1 (Remarks to the Author):

In this manuscript, the authors have explored the CO oxidation process on the binuclear metal site of the heterogeneous Fe/MnO2 catalyst. Sophisticated techniques and theoretic calculations have been employed to characterize the site, analyze its properties and explain the catalytic mechanism. It describes an interesting idea on how to activate oxygen with such a binuclear site in the complex catalysis process. However, the main conclusions are not convincing based on the provided experimental evidence. Thus I could not recommend its acceptance in its current form.

1. The concept of “Binuclear single-atom” in the title is really confusing and frustrating. It is common sense that each atom only has one nucleus. It seems that the term actually means a two-Fe-atom site or bi-atomic or “binuclear iron” site in the text. Why on earth do the authors use the “single-atom” concept?
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3. It’s not a good choice to directly compare the activities of Fe/MnO2 and MnO2 because typically a metal entity possesses a higher activity than an oxide support for the CO oxidation no matter how the metal atoms are dispersed on the oxide.
4. There is not strong evidence to prove the existence of the Fe(O=O)Fe intermediate. A new oxygen species is confirmed by O2-TPD and H2-TPR, but it could be any type of active oxygen species. The O1s XPS in Fig. S8c simply indicates the oxide peak and the wide feature of adsorbed oxygen is not any clue of surface-adsorbed O2 species. Even if the oxygen adsorbs on the surface as O=O, there is no evidence to show that it sits in between two iron atoms.
5. The 1204 cm-1 band in Fig. 3f is supposed to be relating to the Fe(O=O)Fe species. However, the authors should tell the readers that such a decrease in the wavenumber is indeed from the isotopic effect for the Fe(O=O)Fe species. The Fe(O=O)Fe species is non-polar, how could the O-O vibrational mode appear in IR? DFT could help calculate all vibrational modes of the proposed Fe(O=O)Fe species. Such calculations should be included.
6. An additional question about the blank experiment on the structure of the Fe/MnO2 catalyst in Figure 1f: is there any oxygen molecule between the iron atoms at the binuclear site before O2 adsorption takes place? According to the analysis in the manuscript, the active site should be Fe-(Ov)-Fe, then how can the O2 molecule be adsorbed to form Fe(O=O)Fe? The EXAFS result does show the existence of Fe-O and Fe-(O)-Fe. Normally, Mn-O-Mn should be stable in the MnO2 structure. Therefore, Fe-O-Fe should be more stable than Fe-(Ov)-Fe and Fe(O=O)Fe, then why is Fe-O-Fe non-existent in Fe/MnO2?

Reviewer #2 (Remarks to the Author):

The authors claimed that they demonstrated that dual adjacent single Fe atoms anchored on MnO2 can assemble into a binuclear site, which activates molecular oxygen to form an active intermediate species Fe(O=O)Fe for highly efficient CO oxidation. It was concluded that binuclear Fe sites exhibited a stronger O2 activation performance than the conventional surface oxygen vacancy activation sites.
However, the data provided seems not enough to support their claims. I understood that Fe/MnO2 showed better CO oxidation performance compared to pure MnO2 but unfortunately not convinced the formation of binuclear Fe sites and L-H type reaction. The following is the reasons why I consider it is inadequate, including questions and comments. I hope this will help improve the quality of this author's work and contribute further understanding the physics behind this seminal catalytic reaction.

In Fig.1a, TEM with atomic resolution are shown and Fe and Mn atoms were identified by line profile in Fig. 3b. I assume that they were distinguished by the intensity differences of the bright spots from the line profile. If so, I suggest the authors to show TEM for MnO2 to confirm that there is no intensity differences among the bright spots and prove intensity difference is inherently from Fe and Mn in Fe/MnO2. I can see some bright spots on the surface of pure MnO2 in HRTEM of Fig. 3a of the following literature, but their intensities are different.
J. Gao et al./Journal of Catalysis 341 (2016) 82-90.
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Fourie-transformed k-edge EXAFS for Fe2O3 and Fe/MnO2 are quite similar. The possibility of formation Fe2O3 was excluded by comparing the Morlet wavelet transform in Supplementary Fig.3 but the results show no significant difference. The k3-weighted EXAFS can be judged to check the quality of the measured spectra but not shown. It may not be possible to prove that Fe203 is not formed only from the results of this XAFS analysis.

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How can you exclude the possibility of MvK on bare MnO2 surface of Fe/MnO2? Is there any evidence that MvK is hindered by Fe atoms?
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term and share the physical image clearly before it is used for the readership of this multidisciplinary journal.
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on the energetics of the O2 with 1 O bonded to each of the Fe atoms, even if it is indeed higher energy than the O2 bridging the 2 Fe with a single O. Also, based on equation 5, it appears that binding does not include vibrational contributions to the free energy including zero-point energies. Given how close some of the competing binding sites are for the O2, these effects may well shift binding energetics, especially for different binding motifs which should be addressed.

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Response Letter

We thank all three Reviewers for their positive reviews of this manuscripts and the constructive suggestions that help to improve the scientific presentation of this manuscript. Point-by-Point responses to address the concerns raised by the three Reviewers are shown in the following.

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We thank the Reviewer for confirming the important significance of our findings and for approving our extensive catalysis studies, and for making many insightful comments. During the revision, we provided more experimental evidences to support our conclusions.

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Response: We thank the reviewer for the insightful comments. To avoid the confusion, we revised the title into ***Adjacent single-atom irons boosting molecular oxygen activation on MnO_2*** and also corrected the relevant term thoroughly in the paper. The purpose for us to use the concept of single atom is to emphasize the importance of surrounding environment of iron atoms and their interaction with MnO_2 support on the performance of molecular oxygen activation.

2. The existence of binuclear iron sites is demonstrated with the HAADF-STEM images, but unfortunately other sites like single or triple iron atoms cannot be excluded. It's hard to believe that all iron atoms maintain the binuclear configuration. It seems that the manuscript selectively presents a few examples of neighboring binuclear iron atoms. Even so, one can still find that there is at least a single iron atom in Fig. S11 (4). Therefore, the manuscript should provide the statistical distribution of the sites as a function of iron atom number inside.

Response: We thank the Reviewer for the great suggestion. As shown in Figure S15 (Figure S11 in previous submission), single Fe sites were unavoidable during the formation of adjacent iron sites. Therefore, based on the strength of atoms and the distance between adjacent atoms, we statistically analyzed the STEM spectra of 300 atoms in three regions on the surface of three different Fe/MnO_2 catalysts (0.1%, 0.25% and 0.5% Fe/MnO_2) in Figure R1 and Table R1. For 0.25% Fe/MnO_2 shown in the Figure R1b, 1e and Table R1, 80.9% of Fe sites ($n = 2$ and $n > 2$) (n represents the number of adjacent Fe atoms) on the surface were distributed as adjacent Fe sites, and a small number (19.1%) as monatomic Fe site. Obviously, these adjacent Fe sites strongly contributed to the efficient activation of molecular oxygen.

During the revision, Figure R1 and Table R1 were added as the new Supplementary Figure S16 and Table S2 respectively. Meanwhile, we also added more discussions in the revised manuscript on page 8 about the statistical distribution of the sites.

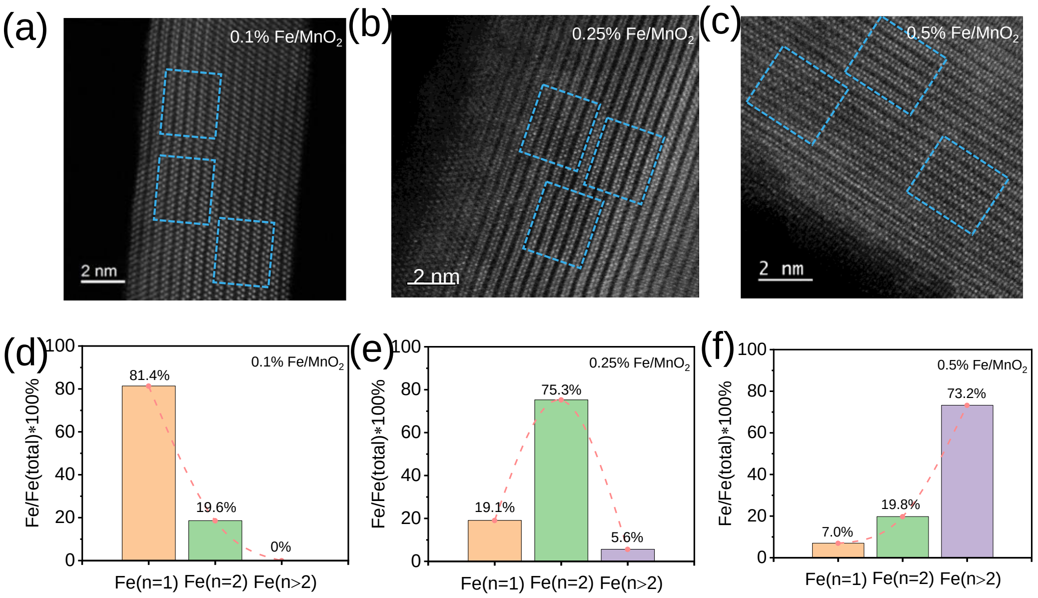

Figure R1. (a-c) STEM images of different Fe/MnO_2 catalysts. The atoms surrounded by the blue dotted box are used for site statistics. (d-f) Statistical results of the number of Fe sites corresponding to different catalysts.

Table R1. Statistical results of different Fe sites and Mn contents of the three catalysts from Figure R1.

	Fe(total)	Fe(n=1)	Fe(n=2)	Fe(n>2)	Mn
0.1% Fe/MnO_2	43	35	8	0	257
0.25% Fe/MnO_2	89	17	67	5	211
0.5% Fe/MnO_2	172	12	34	126	128

n represents the number of adjacent Fe atoms.

3. It’s not a good choice to directly compare the activities of Fe/MnO_2 and MnO_2 because typically a metal entity possesses a higher activity than an oxide support for the CO oxidation no matter how the metal atoms are dispersed on the oxide.

Response: We thank the reviewer for this valuable comment. As the reviewer mentioned, a metal usually possesses a higher activity than an oxide support in CO oxidation reaction. Therefore, we compared the activities of catalysts with different Fe contents (0.1%, 0.25% and 0.5% Fe/MnO_2), and found that 0.25% Fe/MnO_2 exhibited the highest catalytic activity (Figure R2). According to the statistical analysis of iron atoms distribution on the surface of three catalysts (Figure R1 and Table R1), 0.1% Fe/MnO_2 possessed 81.4% of monatomic Fe, while 0.25% Fe/MnO_2 was of 75.3% two adjacent Fe sites. When the content of Fe reached 0.5%, the adjacent Fe sites ($n > 2$) became dominant (73.2%). Obviously, the catalytic activity of Fe/MnO_2 strongly depends on the surrounding environment of iron atoms and their interaction with MnO_2 support.

During the revision, we added the corresponding discussion on page 17 in the revised Supporting Information as follows. ***"We compared the activities of catalysts with different Fe introduction (0.1%, 0.25% and 0.5% Fe/MnO_2), and found that 0.25% Fe/MnO_2 exhibited the highest catalytic activity (Figure S7a). According to the statistical analysis of iron atoms distribution on the surface of three catalysts (Figure S16 and Table S2), 0.1% Fe/MnO_2 possessed 81.4% of monatomic Fe, while 0.25% Fe/MnO_2 was of 75.3% two adjacent single-atom Fe sites. When the content of Fe reached 0.5%, the adjacent Fe sites ($n > 2$) became dominant (73.2%). Obviously, the catalytic activity of Fe/MnO_2 strongly depends on the surrounding environment of iron atoms and their interaction with MnO_2 support."***

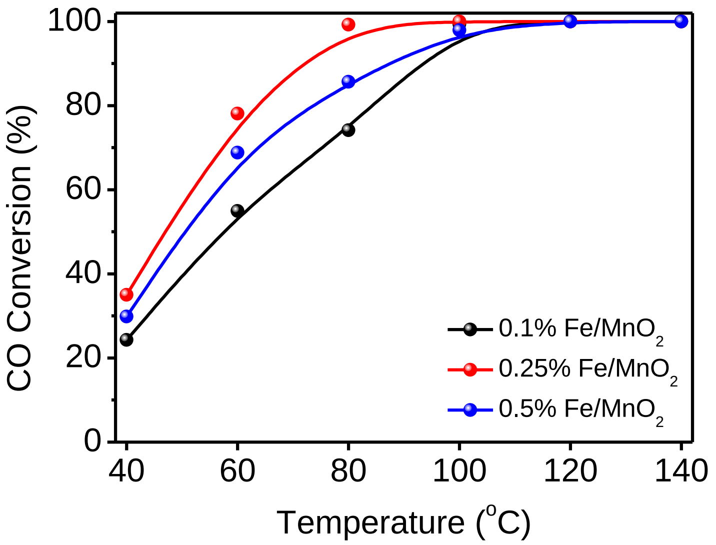

Figure R2. Light-off curves for CO oxidation of different proportions of Fe/MnO_2.

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Response: Thanks a lot for the comment. During the revision, we employed in-situ DRIFTS with $^{18}O_2$ isotope to further confirm the existence of the Fe(O=O)Fe intermediate on the surface of Fe/MnO_2, and found that the characteristic peak of 1204 cm^{-1} shifted to the direction of low wavenumber owing to isotopic effect (Figure R3), suggesting this peak was associated with O_2. As for MnO_2, the in-situ DRIFTS with $^{16}O_2$ did not display any peaks near 1204 cm^{-1} (Figure R4). Accordingly, the adsorption site of O_2 was related to Fe species. In light of the calculation results (Figure R5) that O_2 was absorbed on the two adjacent Fe sites (-2.00 eV) with the highest adsorption energy, the Fe(O=O)Fe was the most favorable adsorption configuration. Furthermore, we calculated the infrared spectra of Fe/MnO_2 and Fe/MnO_2 with O_2 adsorption in the configuration of Fe(O=O)Fe (Figure R6). In the simulated infrared spectrum of Fe/MnO_2 with O_2 adsorption, a new characteristic peak appeared near 1200 cm^{-1}. We also performed the EXAFS fitting of Fe(O=O)Fe, which were highly coincident with the experimental results (Figure R7). Therefore, we believed that O_2 was adsorbed to the two adjacent Fe sites with the binuclear configuration and was thus activated.

During the revision, Figure R5 was modified as the new Supplementary Figure S13, Figure R6 was added as a new Figure 3c in the revised manuscript and the corresponding discussion was added on page 8 in the revised manuscript as follows.

"Furthermore, we simulated the infrared spectra of Fe/MnO_2 and Fe/MnO_2 with O_2 adsorption by DFT calculation (Figure 3c). In the simulated infrared spectrum of Fe/MnO_2 with O_2 adsorption, a new characteristic peak appeared near 1200 cm^{-1}, which was consistent with the experiment results."

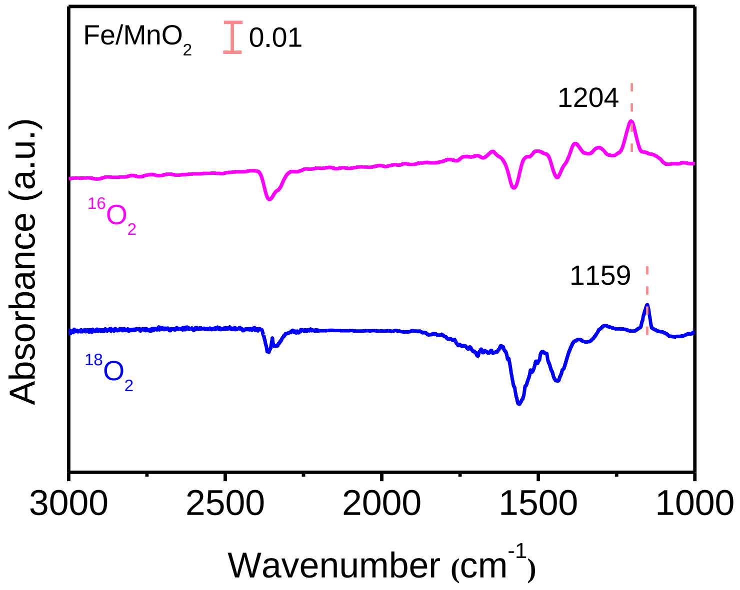


Figure R3. In situ DRIFTS of $^{18}O_2$ isotope over Fe/MnO$_2$ in the out-line system.

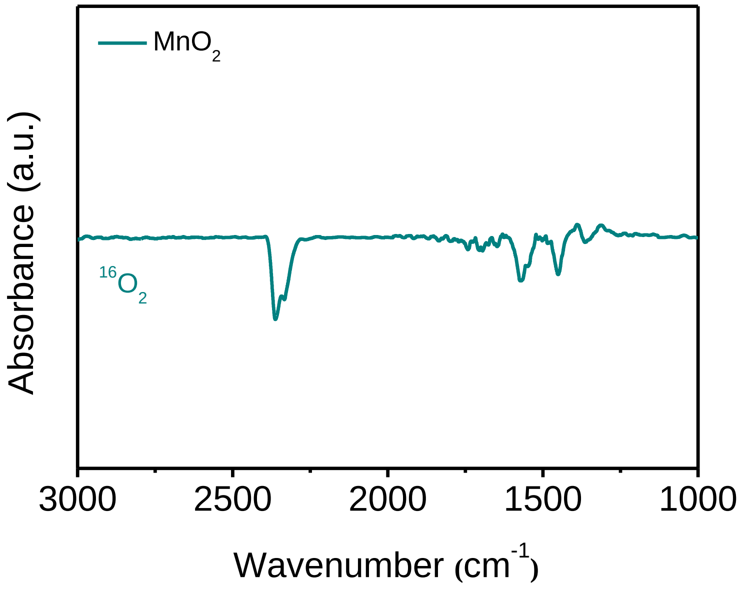
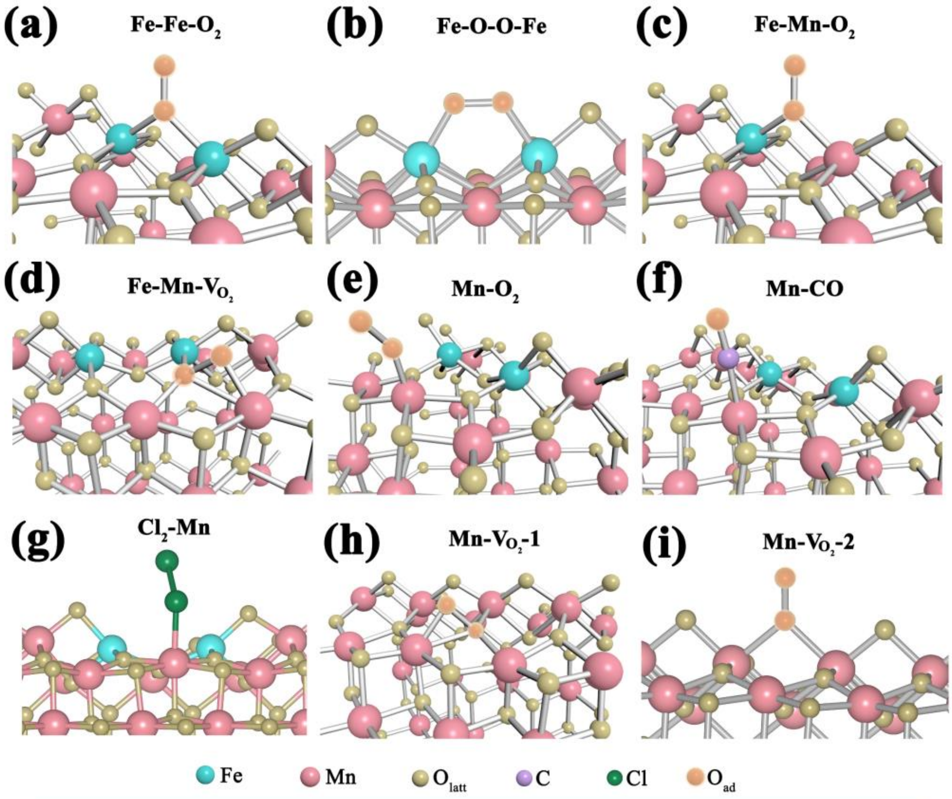


Figure R4. In situ DRIFTS of $^{16}O_2$ over MnO$_2$ in the out-line system.



Configuration	a	b	c	d	e	f	g	h	i
Adsorption Energy (eV)	-2.00	-1.47	-1.82	-0.83	-1.66	-2.15	-3.11	-2.39	-1.69

Figure R5. The stable configurations of (a-e) O_2, (f) CO and (g) Cl_2 adsorbed at the different sites of Fe/MnO_2 surface, and O_2 adsorbed in (h) the oxygen vacancy or (i) bi-manganese sites of MnO_2. The corresponding adsorption energy with zero-point energy correction is listed in the table of the picture.

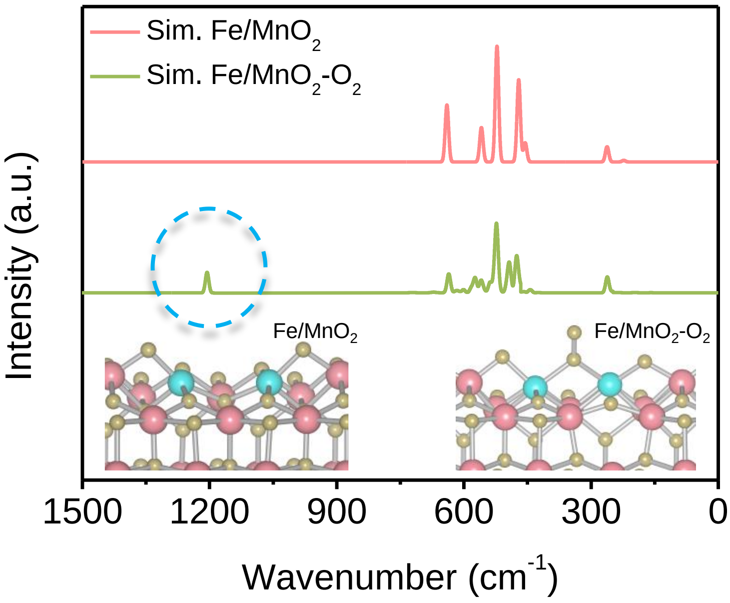


Figure R6. Simulated infrared spectra of Fe/MnO$_2$ and Fe/MnO$_2$ with O$_2$ adsorption. The bottom of the picture was the structure of the different species.

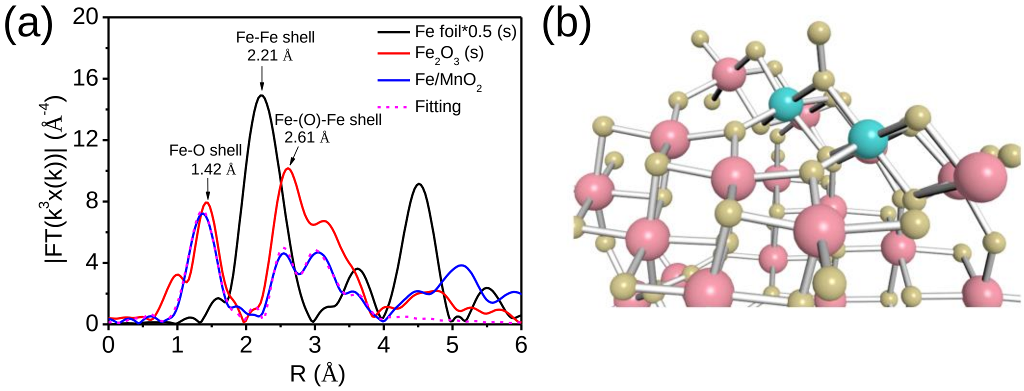


Figure R7. (a) Fourier-transformed K-edge EXAFS spectra in R-space of Fe (without phase correction) and the fitting of Fe/MnO$_2$ structure in (b).

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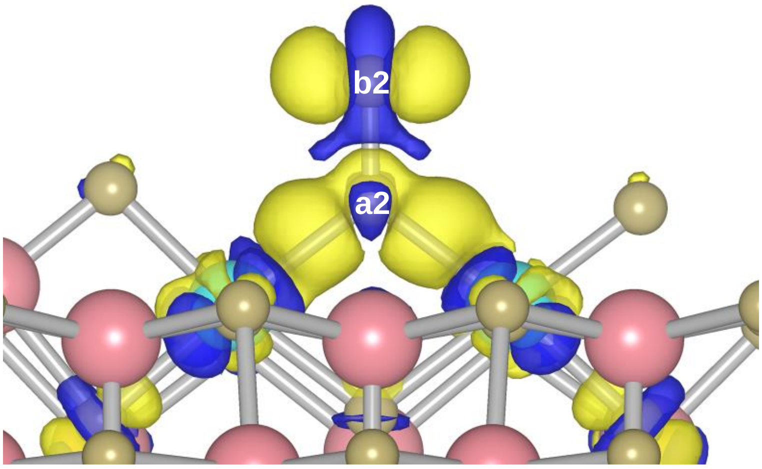
Response: We thank the reviewer for this valuable advice. The simulated infrared spectra (Figure R6) confirmed that the 1204 cm^{-1} band in Figure 2f was related to the Fe(O=O)Fe species. Previously studies revealed that the decrease in the wavenumber of in-situ DRIFTS with $^{18}O_2$ was arisen from the isotopic effect [please see *Nat. Catal.* 2, 916-924 (2019)], which was added on page 7 in the revised manuscript as follows. ***"When $^{16}O_2$ was replaced by $^{18}O_2$, this characteristic peak shifted from 1204 cm^{-1} to the lower wavenumber of 1159 cm^{-1} due to the isotopic effect (Figure 3a), indicating that this peak was closely related to the new active oxygen species generated via O_2 activation on Fe/MnO_2 [22]."***

Bader charge calculation results revealed the two oxygen atoms had different charges (-0.37 and -0.06) after an oxygen molecule was adsorbed on the two adjacent Fe sites with end-on mode (Figure R8). The different charges constantly changed the dipole moment of O_2 in the vibration process, accounting for the infrared characteristic absorption peak of Fe(O=O)Fe. During the revision, we simulated infrared spectra of Fe/MnO_2 and Fe/MnO_2 with O_2 adsorption by DFT calculation. As expected, a new characteristic peak appeared near 1200 cm^{-1} for Fe/MnO_2 with O_2 adsorption (Figure R6), consistent with the experimental results.



Fe/MnO_2	a2	b2
Bader Charge	-0.37	-0.06

Figure R8. The difference charge density of O_2 adsorbed on Fe/MnO_2. Different oxygen atoms from adsorbed oxygen species were labeled as a and b, and corresponding Bader charge was recorded in the bottom of charge density map. The charge density of yellow and blue represents the concentrated and scarce electrostatic potential scale respectively.

6. An additional question about the blank experiment on the structure of the Fe/MnO$_2$ catalyst in Figure 1f: is there any oxygen molecule between the iron atoms at the binuclear site before O$_2$ adsorption takes place? According to the analysis in the manuscript, the active site should be Fe-(Ov)-Fe, then how can the O$_2$ molecule be adsorbed to form Fe(O=O)Fe? The EXAFS result does show the existence of Fe-O and Fe-(O)-Fe. Normally, Mn-O-Mn should be stable in the MnO$_2$ structure. Therefore, Fe-O-Fe should be more stable than Fe-(Ov)-Fe and Fe(O=O)Fe, then why is Fe-O-Fe non-existent in Fe/MnO$_2$?

Response: We thank the reviewer for the valuable comments. We would like to answer the comments as follows.

(1) The DFT calculation results demonstrated that O$_2$ was absorbed on the two adjacent Fe sites (-2.00 eV) with the highest adsorption energy, indicating that the Fe(O=O)Fe was the most favorable adsorption configuration (Figure R5a). Regarding that the catalyst after hydrothermal reaction was calcined in air atmosphere during the preparation process of Fe/MnO$_2$, we believe that oxygen molecules might be adsorbed between the two adjacent Fe sites before O$_2$ adsorption.

(2) The formation of Fe(O=O)Fe might be related to the synthesis method of the catalyst. To verify this assumption, we conducted ATR measurements of Fe/MnO$_2$ synthesized at different temperatures (Figure R9). The characteristic peaks of ferric oxalate (757, 812 and 1255 cm^{-1}) appeared in the catalysts synthesized at 80 ^{o}C, which were weakened along with the further increase of the synthesis temperatures. In combination with Figure S25 and S26, the iron species existed in the precursor solution with the form of iron oxalate complex. With the increase of hydrothermal temperature, [MnO$_6$] structural units appeared in priority, resulting in the formation of the periodic structure of MnO$_2$. Then, the ferric oxalate was gradually decomposed

into CO_2, leaving Fe atoms on the surface of MnO_2. Regarding that oxalate was excessive and the reaction was in a reductive environment [please see *J. Hazard. Mater.*, 262, 701-708 (2013) and *Environ. Sci. Technol.*, 53, 6444-6453 (2019)], oxygen vacancies were more easily generated on the catalyst surface. Therefore, we believe that the two adjacent sites possessed the Fe-(O_V)-Fe configuration and thus formed Fe(O=O)Fe species after calcination in the air atmosphere,.

(3) We also simulated the infrared spectrum of Fe/MnO_2 with Fe-O-Fe structure, and did not find the appearance of characteristic peak near 1200 cm^{-1} (Figure R10). Thus, more active Fe(O=O)Fe can be obtained through the hydrothermal method of oxalate-assisted chelation coordination , even though Fe-O-Fe is more stable.

During the revision, Figure R9 was added as new Supplementary Figure S24.

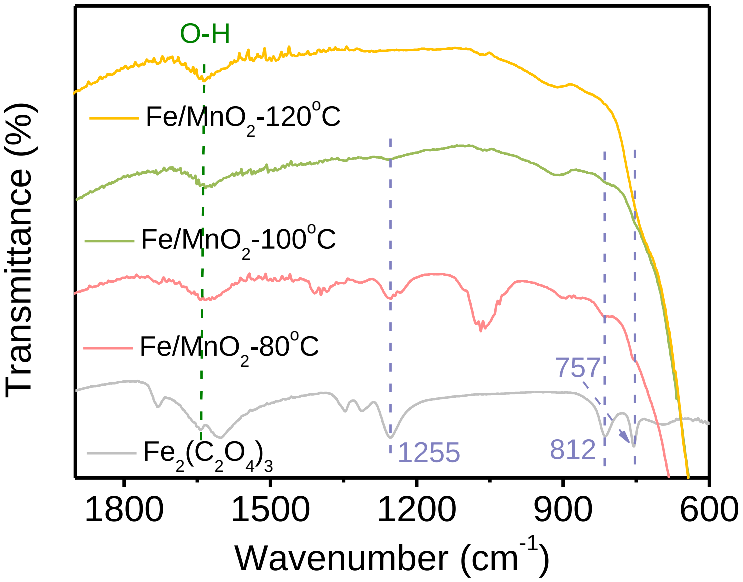


Figure R9. ATR spectra of standard $Fe_2(C_2O_4)_3$ and Fe/MnO_2 synthesized from at different temperatures.

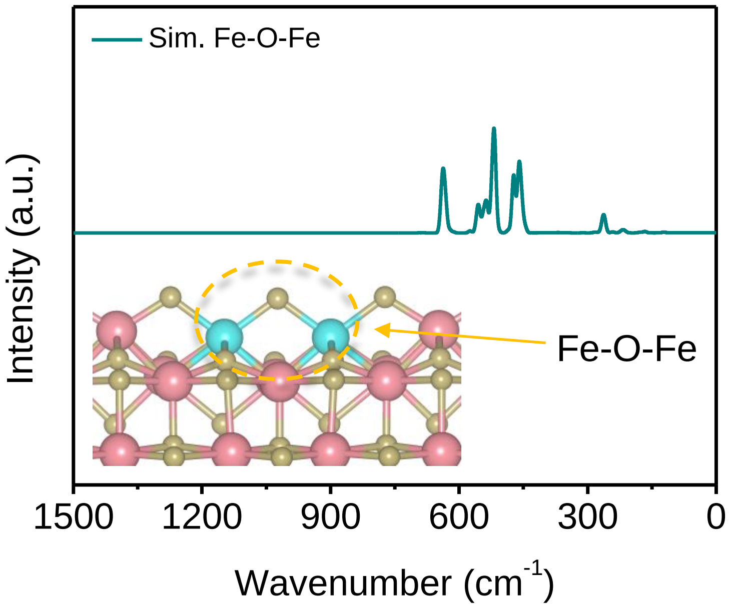


Figure R10. Simulated infrared spectrum of Fe/MnO$_2$ with Fe-O-Fe structure. The bottom of the picture was the structure of the different species

Reviewer #2 (Remarks to the Author):

The authors claimed that they demonstrated that dual adjacent single Fe atoms anchored on MnO_2 *can assemble into a binuclear site, which activates molecular oxygen to form an active intermediate species Fe(O=O)Fe for highly efficient CO oxidation. It was concluded that binuclear Fe sites exhibited a stronger* O_2 *activation performance than the conventional surface oxygen vacancy activation sites.*

However, the data provided seems not enough to support their claims. The following is the reasons why I consider it is inadequate, including questions and comments. I hope this will help improve the quality of this author's work and contribute further understanding the physics behind this seminal catalytic reaction.

Thank you for your summary. We appreciate your efforts in reviewing our manuscript and have revised the manuscript accordingly to support our conclusions as strongly as possible.

In Fig.1a, TEM with atomic resolution are shown and Fe and Mn atoms were identified by line profile in Fig. 3b. I assume that they were distinguished by the intensity differences of the bright spots from the line profile. If so, I suggest the authors to show TEM for MnO_2 *to confirm that there is no intensity differences among the bright spots and prove intensity difference is inherently from Fe and Mn in Fe/*MnO_2*. I can see some bright spots on the surface of pure* MnO_2 *in HRTEM of Fig. 3a of the following literature, but their intensities are different.*

J. Gao et al./Journal of Catalysis 341 (2016) 82-90.

I also suggest showing line profile for longer distance and calculating the Fe coverage to see if it is consistent to the amount of introduced Fe. In some areas, three or more bright spots appear to be lined up.

Response: We thank the reviewer for this constructive advice and would like to reply the comments as follows.

(1) We distinguished Mn and Fe atoms by the intensity difference and the distance between the atoms from HAADF-STEM, because the intensity of Fe is stronger than that of Mn. Meanwhile, DFT calculation results revealed the distance between Fe-Fe

was 3.1 Å, longer than that 2.7 Å of Fe-Mn. Referring to the remarkable article [*J. Catal.*, 341, 82-90 (2016)], we performed STEM test on pure MnO_2 (Figure R11). The results revealed that the intensity and the distance of 2.9 Å between the atoms were in accordance with the theoretical calculation model of MnO_2.

(2) Based on the strength of atoms and the distance between adjacent atoms, we statistically analyzed the STEM spectra of 300 atoms in three regions on the surface of three different Fe/MnO_2 catalysts (0.1%, 0.25% and 0.5% Fe/MnO_2) in Figure R1 and Table R1. For 0.25% Fe/MnO_2, 89 of 300 atoms on the surface were counted as Fe atoms, and others as Mn atoms. According to the model structure of Fe/MnO_2 (Figure R12), the height of the monolayer atoms is 2.63 Å (h). The TEM results displayed that the thickness of the nanorods was about 19.7 nm (H), consistent with the literature [*ACS Catal.* 8, 3435-3446 (2018)]. On the basis of calculation formulas (1-5), the mass fraction of Fe was 0.46%, very close to the ICP test results (0.3%), if the impurities adsorbed on the surface were ignored. These results have demonstrated that Fe is distributed as a single atom on the surface of Fe/MnO_2, and it is feasible to distinguish Mn and Fe atoms according to the differences in strength and distance.

$$m_{Fe} = \frac{n_{Fe} \times M_{Fe}}{N_A} \tag{1}$$

$$m_{Mn} = \frac{n_{Mn} \times M_{Mn}}{N_A} \tag{2}$$

$$m_O = \frac{2 \times (n_{Mn} + n_{Fe}) \times M_O}{N_A} \tag{3}$$

$$N = \frac{H}{h} \tag{4}$$

$$W_{Fe} = \frac{2 \times m_{Fe}}{2 \times (m_{Fe} + m_{Mn} + m_O) + 300 \times m_{MnO_2} \times N} \tag{5}$$

Where m represents the mass of different element; N is the number of atoms; M is the relative atomic mass; N_A is the Avogadro constant; H is the thickness of catalyst, which is counted by TEM test results. h represents the height of single-layer MnO_2, which comes from the structural optimization model; N is the number of layers; W_{Fe}

is the mass fraction of Fe;

During the revision, Figure R11 and R12 were added as the new Supplementary Figure S14 and S17 respectively. We also cited this relevant literature [J. Catal., 341 82-90 (2016)] as Ref. 23 and added the corresponding discussion on page 18 in the revised Supporting Information as follows. ***"Based on the strength of atoms and the distance between adjacent atoms, we statistically analyzed the STEM spectra of 300 atoms in three regions on the surface of three different Fe/MnO$_2$ catalysts (0.1%, 0.25% and 0.5% Fe/MnO$_2$) in Figure S16 and Table R2. For 0.25% Fe/MnO$_2$, 89 of 300 atoms on the surface were counted as Fe atoms, and others as Mn atoms. According to the model structure of Fe/MnO$_2$ (Figure S17), the height of the monolayer atoms is 2.63 Å (h). The TEM results displayed that the thickness of the nanorods was about 19.7 nm (H), consistent with the literature [4]. On the basis of calculation formulas (5-9), the mass fraction of Fe was 0.46%, very close to the ICP test results (0.3%), if the impurities adsorbed on the surface were ignored. These results have demonstrated that Fe is distributed as a single atom on the surface of Fe/MnO$_2$, and it is feasible to distinguish Mn and Fe atoms according to the differences in strength and distance."***

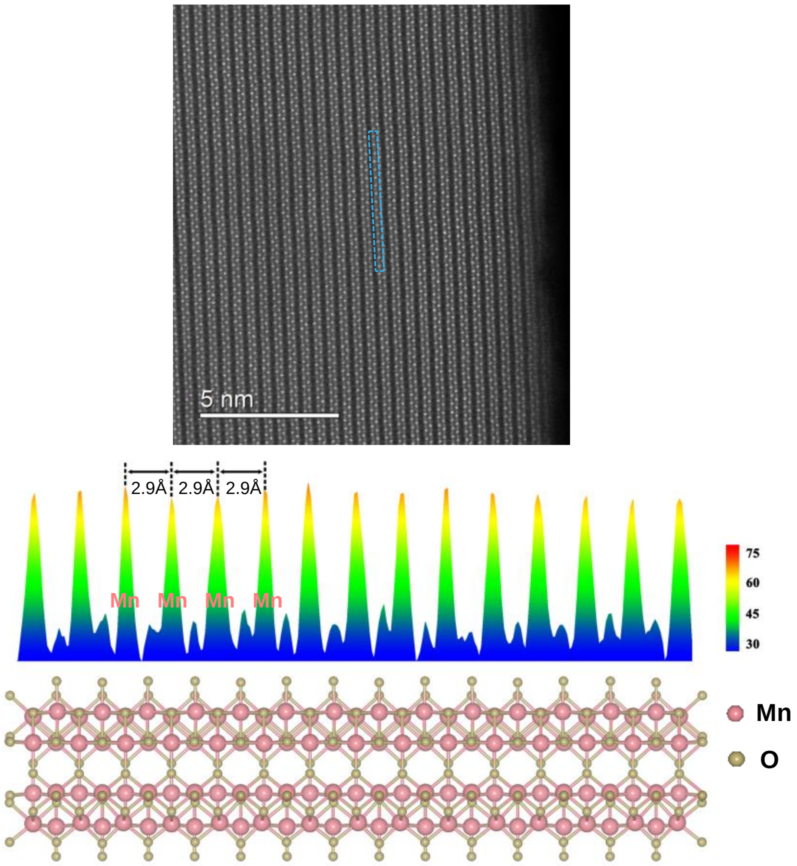


Figure R11. STEM image of MnO_2 (top), intensity surface plot from blue dashed rectangle (middle) and the corresponding structural model (bottom).

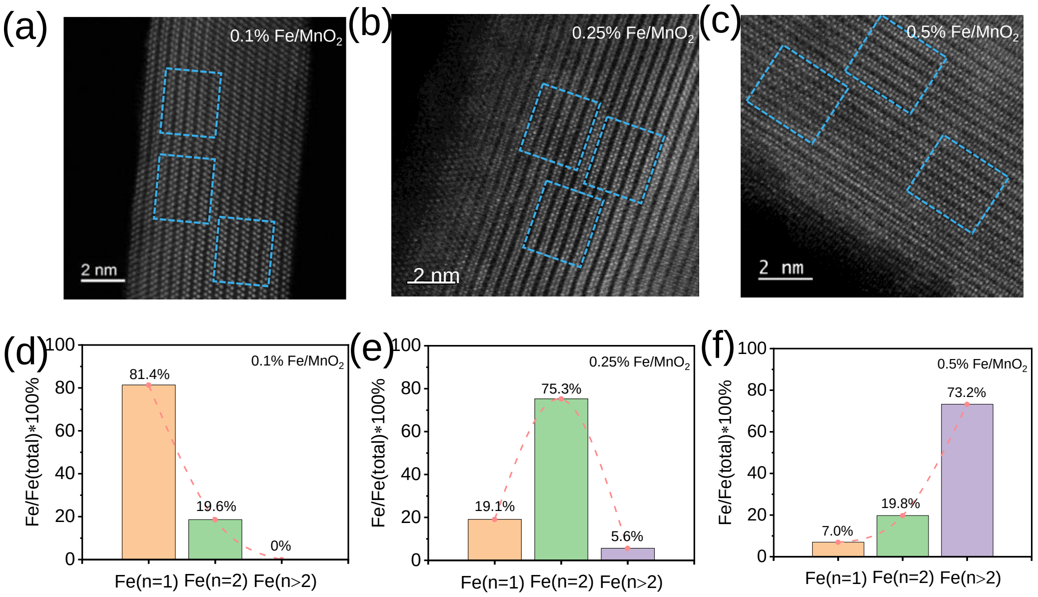


Figure R1. (a-c) STEM images of different Fe/MnO_2 catalysts. The atoms surrounded by the blue dotted box will be used for site statistics. (d-f) Statistical results of the number of Fe sites corresponding to different catalysts.

Table R1. Statistical results of different Fe sites and Mn contents of the three catalysts from Figure R1.

	Fe(total)	Fe(n=1)	Fe(n=2)	Fe(n>2)	Mn
0.1% Fe/MnO_2	43	35	8	0	257
0.25% Fe/MnO_2	89	17	67	5	211
0.5% Fe/MnO_2	172	12	34	126	128

n represents the number of adjacent Fe atoms.

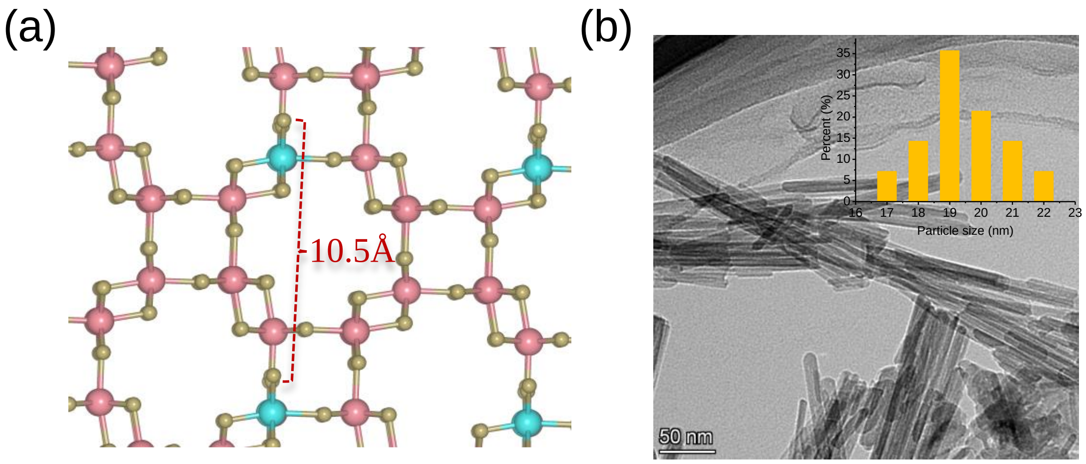


Figure R12. (a) The structural model and (b) TEM spectrum of Fe/MnO_2. Particle size was counted according to TEM result.

XAFS was taken for Fe foil (metallic Fe), Fe_2O_3 (Fe^{3+}) and Fe/MnO_2 and spectrum of Fe/MnO_2 is almost the same to that of Fe_2O_3. I suggest authors to discuss oxidation state of Fe based on the result of XPS of Fe on Fe/MnO_2 with literatures and Bader charge.

Fourie-transformed k-edge EXAFS for Fe_2O_3 and Fe/MnO_2 are quite similar. The possibility of formation Fe_2O_3 was excluded by comparing the Morlet wavelet transform in Supplementary Fig.3 but the results show no significant difference. The k3-weighted EXAFS can be judged to check the quality of the measured spectra but not shown. It may not be possible to prove that Fe_2O_3 is not formed only from the *results of this XAFS analysis.*

Response: Thank you for your kind comments and helpful suggestions. We used ammonium oxalate and iron nitrate to synthesize Fe_2O_3, and measured the Fe 3d XPS spectra of pure Fe_2O_3 and Fe/MnO_2 (Figure R13). It was found that the characteristic peak of Fe/MnO_2 had lower binding energy (710.6 eV) than that (711.4 eV) of Fe_2O_3. Meanwhile, Bader charge calculation results revealed that Fe on Fe/MnO_2 possessed more electrons than that of Fe_2O_3, consistent with the results of XANES absorption (Figure R14). Furthermore, the statistical results of Fe atoms distributed on the surface of 0.25% Fe/MnO_2 from STEM spectrum (0.46%) matched with the result from ICP test (0.3%). These results ruled out the formation of Fe_2O_3 in the Fe/MnO_2. k3-weighted EXAFS was shown in Fig. R15 (Figure S3 of revised Supporting Information).

During the revision, Figure R13 and R15 were added as new Figure S6 and Figure S3 in the revised Supporting Information respectively, and more discussion was added on page 5 in the manuscript as follows. ***"We also compared the Fe 3d XPS spectra of Fe_2O_3 and Fe/MnO_2 (Figure S6), and found that the characteristic peak of Fe/MnO_2 had lower binding energy (710.6 eV) than that (711.4 eV) of Fe_2O_3. Meanwhile, Bader charge calculation results revealed that Fe on Fe/MnO_2 possessed more electrons than that of Fe_2O_3, consistent with the results of XANES absorption (Figure 1d)."***

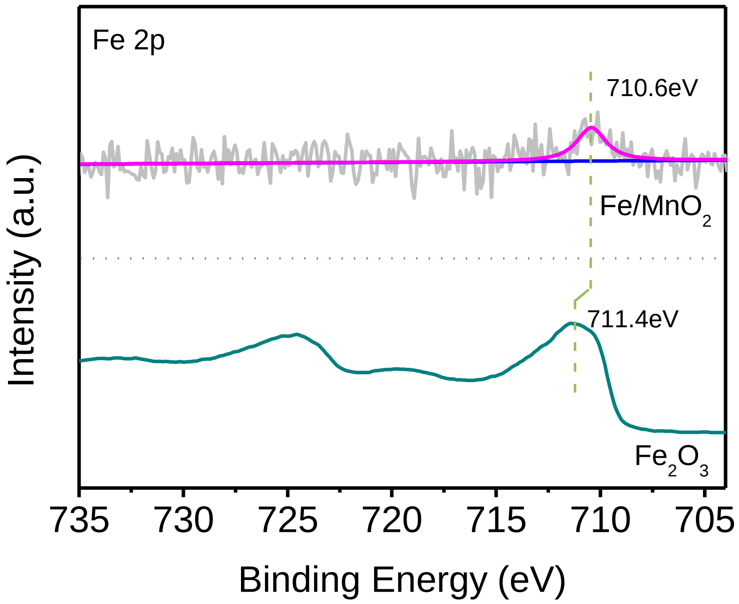


Figure R13. XPS spectrum of Fe2p in Fe/MnO$_2$ and Fe$_2$O$_3$ sample.

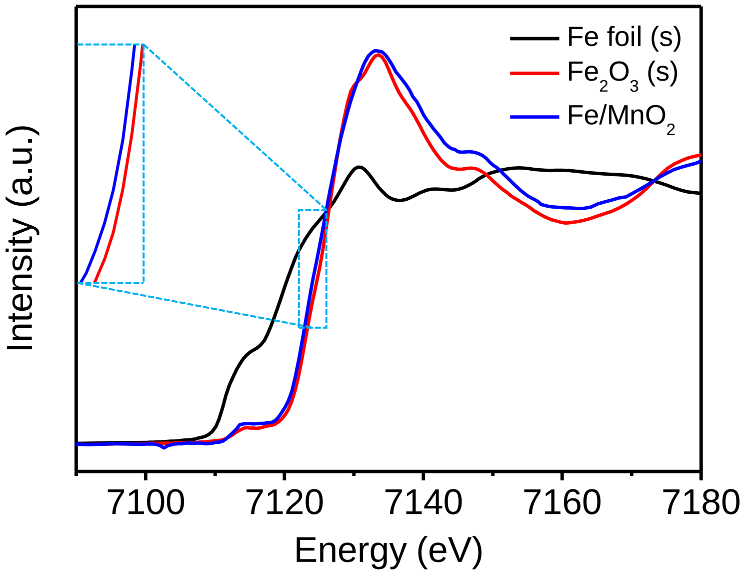


Figure R14. Normalized XANES spectra of Fe.

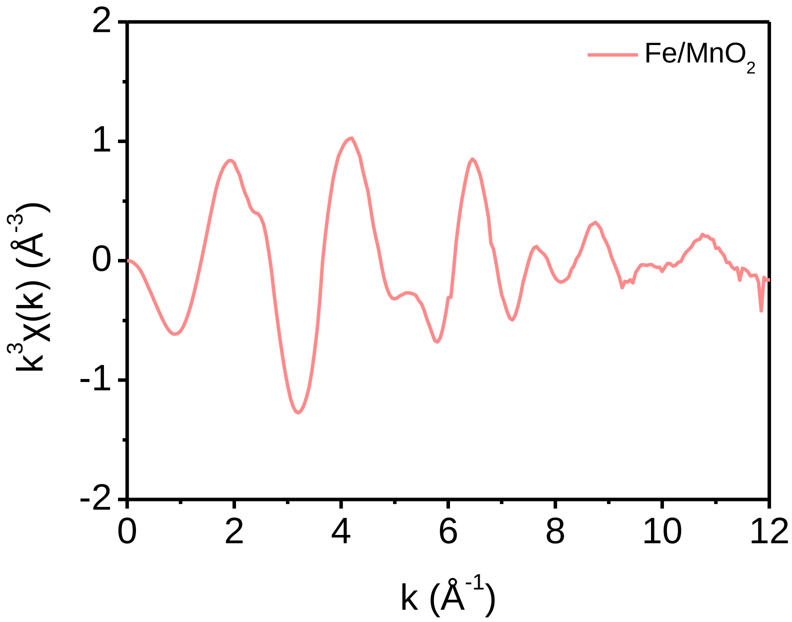


Figure R15. k3-weighted EXAFS spectrum of Fe/MnO_2 sample.

Peaks in Fig 3a is too small to see.

Response: Thanks for the suggestions. We enlarged the peaks in Figure R3 for better view (Figure 3a in the revised manuscript).

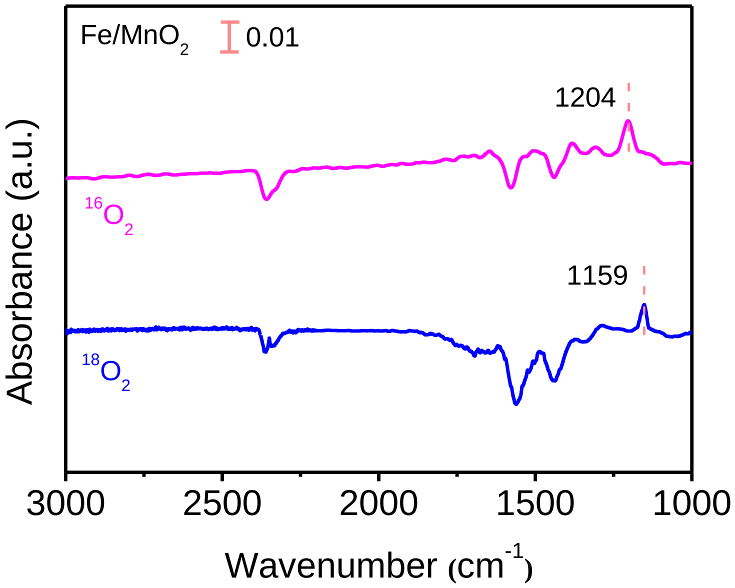


Figure R3. In situ DRIFTS of $^{18}O_2$ isotope over Fe/MnO_2 in the out-line system.

How can you exclude the possibility of MvK on bare MnO_2 surface of Fe/MnO_2? Is *there any evidence that MvK is hindered by Fe atoms?*

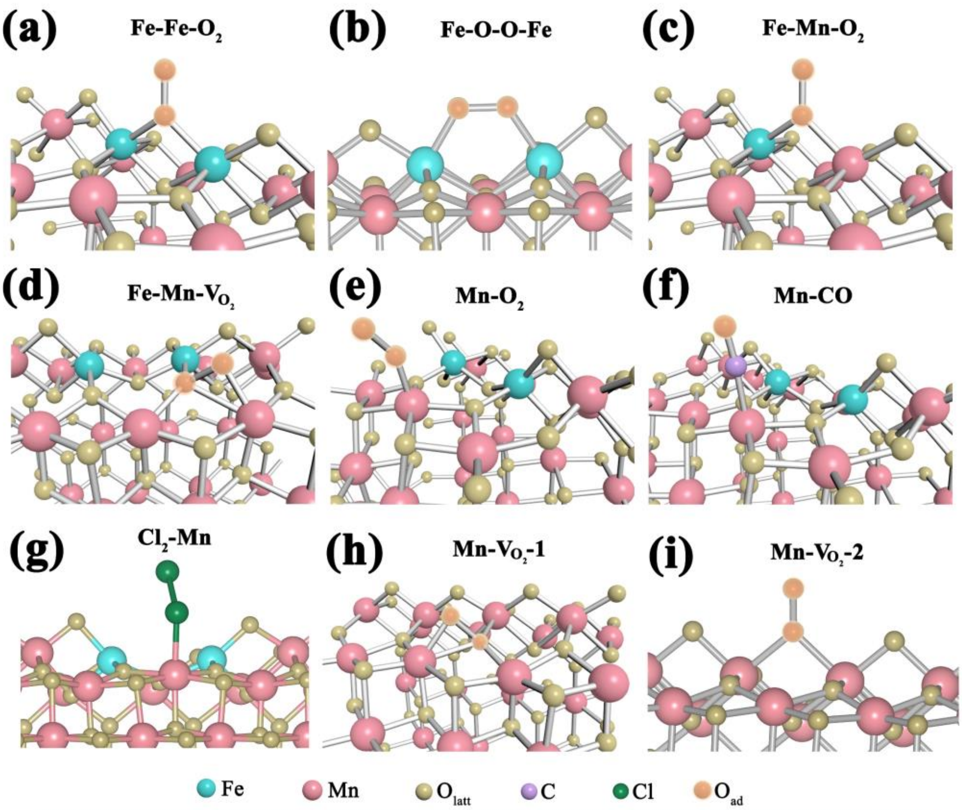
The Fe(O=O)Fe was suggested to the preferentially adsorbed configuration of O_2 since the adsorption energy is high, however, in the calculation in Supplementary Fig .10, Mn(O=O)Mn was not calculated.

Response: We thank the reviewer for these valuable questions and would like to reply the comments as follows.

(1) We adopted DFT calculation to check why the MvK mechanism on MnO_2 surface was hindered by Fe atoms. First of all, O_2 located at the unsaturated Fe sites possessed a higher energy (-2.00 eV in Figure R5a) than that at the oxygen vacancy (-0.83 eV in Figure R5d). Then, the calculation results of the transition state revealed that the energy (0.19 eV) for CO reacting with O_2 adsorbed on the two adjacent Fe sites was lower than that (0.37 eV) of O_2 adsorbed in the oxygen vacancy (Figure R16). Therefore, the MvK mechanism on bare MnO_2 was inhibited by the high energy demand.

(2) In accordance with the reviewer's suggestion, we calculated the oxygen adsorption energy (-1.69 eV) of Mn(O=O)Mn configuration (Figure R5i), which was lower than that (-2.00 eV) of Fe(O=O)Fe.

During the revision, Figure R16 was added as the new Supplementary Figure S29 and the corresponding discussion was added on page 13 in the revised manuscript as follows. ***"Furthermore, we also calculated the energy of CO reacting with O_2 on different sites. The calculation results of the transition state revealed that the energy (0.19 eV) for CO reacting with O_2 adsorbed on the adjacent Fe sites was lower than that (0.37 eV) of O_2 adsorbed on the Vo referring to Figure S29. Therefore, the MvK mechanism on bare MnO_2 could be inhibited by the high energy demand."***



Configuration	a	b	c	d	e	f	g	h	i
Adsorption Energy (eV)	-2.00	-1.47	-1.82	-0.83	-1.66	-2.15	-3.11	-2.39	-1.69

Figure R5. The stable configurations of (a-e) O_2, (f) CO and (g) Cl_2 adsorbed at the different sites of Fe/MnO_2 surface, and O_2 adsorbed in (h) the oxygen vacancy or (i) bi-manganese sites of MnO_2. The corresponding adsorption energy with zero-point energy correction is listed in the table of the picture.

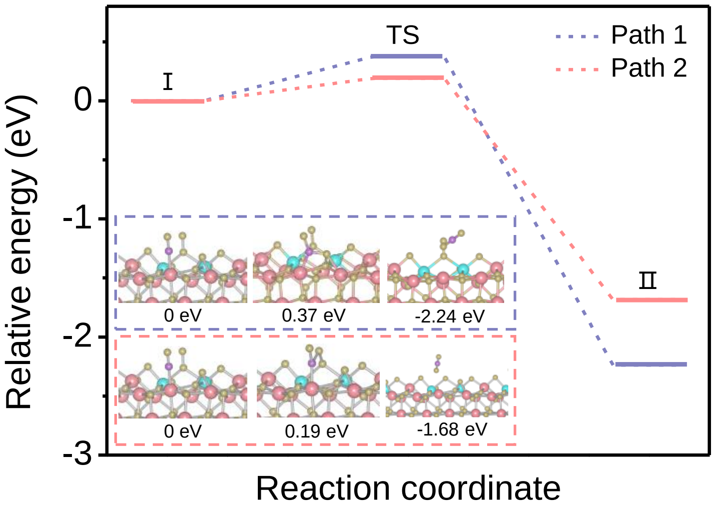


Figure R16. Energy profiles of CO reacted through the different path in Fe/MnO_2. The optimized structures of initial states (I), transition states (TS) and final states (II) are listed in the dotted box, and the relative energy is recorded below the corresponding structure.

What is the meaning of "molecular oxygen activation" and "activation behavior of oxygen" in line 32 and 184? Is it mentioning low dissociation energy of oxygen molecules? I suggest the authors define the term and share the physical image clearly before it is used for the readership of this multidisciplinary journal.

Response: We appreciate the reviewer for these kind suggestions. In the original manuscript, both molecular oxygen activation and activation behavior of oxygen corresponded to weakening O=O double bond, reducing dissociation energy of oxygen molecule and facilitating oxygen to participate in the reaction process more easily. The diagram of molecular oxygen activation was shown in Figure R17. We added more description for better understanding of this term.

During the revision, Figure R17 was added as the new Supplementary Figure S1 and the corresponding discussion about the term of molecular oxygen activation was added on page 2 in the revised manuscript and page 2 in the Supporting Information as follows. ***"Molecular oxygen activation is a continuous process of adsorption and dissociation of O_2 on the catalyst surface. The process relies on the transfer of***

***electrons from the surface of catalyst to the O_2 to weaken the oxygen-oxygen double bond. Meanwhile, the structure of the adsorption site on the catalyst surface plays an important role in the activation of O_2.* [Chem. Rev., 118, 2816-2862 (2018); *Nat Commun.* 12, 2741 (2021)]"**

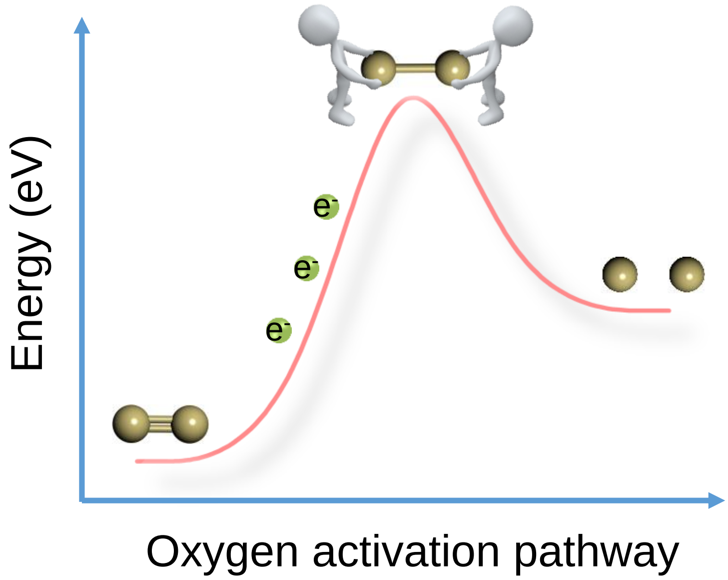


Figure R17. Diagram of molecular oxygen activation.

In line 24, in introductory part, author described that high concentration of oxygen in air or high temperature will inevitably lead to the refilling of oxygen vacancy by referencing ORR study and not CO oxidation. I don't think this is appropriate citation. There are many studies for oxygen vacancy involved CO oxidation studies. I suggest authors to present discussions based on more relevant literatures. For the same reasons, reference 1 to 3 seems inappropriate (they are electrochemical ORR studies and there should be more relevant references).

Response: We thank the reviewer for the valuable suggestion. We deleted references 1-4 from the original manuscript and replaced them with new references 7-9 [*J. Am. Chem. Soc.* 140, 4580-4587 (2018); *ACS Catal.* 9, 9751-9763 (2019); *ChemCatChem* 9, 1119-1127 (2017)]. These references offer us deeper atomic-level insights into the relationship between oxygen vacancy and molecular oxygen activation, promoting CO oxidation.

Injection of Cl_2 was performed. Is it necessarily be Cl_2? Why Cl_2? I recommend authors to add explanation why this way is good for investigating/identifying the CO oxidation mechanism, probably with citing some articles.

Response: We thank the reviewer for these valuable comments. Chlorine is well known for its high electron density and strong adsorption properties [*J. Am. Chem. Soc.*, 2012, 134, 20160−20168]. Some literatures reported that chlorine was prone to form strong adsorption with metal sites on the catalyst surface during the catalytic reaction, leading to catalyst deactivation [please see *Chem. Rev.*, 2019, 119, 4471−4568; *Environ. Sci. Technol.*, 2021, 55, 4007−4016]. Even after oxygen adsorption, Cl_2 could cover the surface of MnO_2 and firmly occupied the adsorption sites of CO. Furthermore, Cl_2 has a stronger adsorption capacity at unsaturated Mn sites than CO (-3.11 eV for Cl_2 versus -2.15 eV for CO), accounting for the design idea of the experiment. Therefore, we used Cl_2 to study the reaction mechanism in this study.

During the revision, we cited the related works as Refs. 26-28 and added more discussion on page 22 in the Supporting Information as follows. ***"Chlorine is well known for its high electron density and strong adsorption properties. Some literatures reported that chlorine was prone to form strong adsorption with metal sites on the catalyst surface during the catalytic reaction, leading to catalyst deactivation [5, 6]. Even after oxygen adsorption, Cl_2 could cover the surface of MnO_2 and firmly occupied the adsorption sites of CO. Furthermore, Cl_2 has a stronger adsorption capacity at unsaturated Mn sites than CO (-3.11 eV for Cl_2 versus -2.15 eV for CO), accounting for the design idea of the experiment. Therefore, we used Cl_2 to study the reaction mechanism in this study."***

In Supplementary Fig. 11 STEM images were shown but two of them are labeled the same. I recommend that you carefully check the other data to make sure there are no misrepresentations. Unit error was found in Line 108 and it should be 167 ^{o}C, not cm^{-1}.

Response: We are sorry for the typo error and carefully checked the manuscript thoroughly.

In Supplementary Fig. 6, fitted light off curve for MnO_2 *is awkward. Fitting needs to be performed based on the provided data and how you fit needs to be mentioned with reliability factor.*

Response: We appreciate the reviewer for the valuable comment. Figure R18 corresponds to the activity spectrum after the normalization of specific surface area. The relation between $C/(C_0*S)$ and T was used to plot the spectrum, rather than the result of kinetic curve fitting.

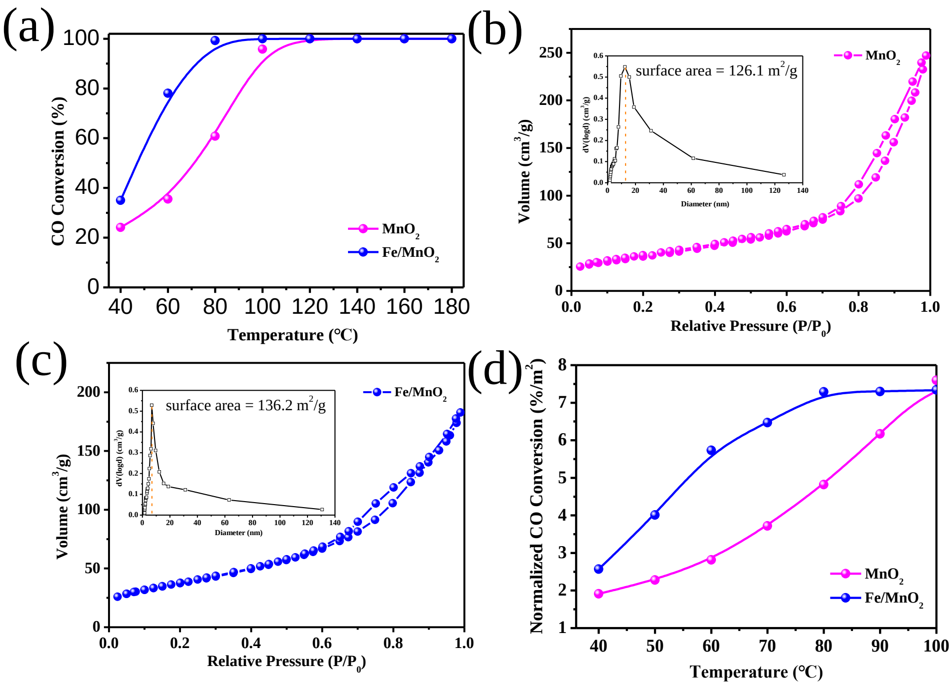


Figure R18. (a) Light-off curves of CO oxidation over Fe/MnO_2 and MnO_2. Nitrogen adsorption/desorption isotherm plots of (b) MnO_2 and (c) Fe/MnO_2 (the insets of a and b showed the pore size distribution). (d) CO catalytic performance of the MnO_2 and Fe/MnO_2 normalized by BET surface area.

Reviewer #3 (Remarks to the Author):

In this work, the authors report on a novel "single-atom" binuclear iron site embedded in a MnO_2 *host lattice. Overall, this work is of very high quality and the findings are corroborated with theoretical study. This kind of earth-abundant material may well serve as the next generation of catalyst for a variety of chemical technologies and this type of fundamental study will be valuable in identifying paths forward in both improving and utilizing such structures. A few minor suggestions that might improve this manuscript:*

We thank the reviewer for the valuable and constructive comments and carefully revised the manuscript.

1) While I understand the usage in comparison to previous work, the portion of the title "Binuclear single-atom irons" is a bit problematic as the binuclear and plural of iron both seem to contradict the "single-atom" term. This term is of course somewhat problematic for all "single-atom" sites since local structure can strongly influence key binding sites but even more so here where 2 distinct atoms are serving as the localized active site. A similar issue occurs at the end of the discussion on page 12 where the term "monatomic binuclear active sites" is used.

Response: Thank you for your helpful comments. We agree with the reviewer's suggestion. To avoid the confusion, we revised the title into ***Adjacent single-atom irons boosting molecular oxygen activation on*** MnO_2 and also corrected the relevant term thoroughly in the paper.

2) Oxygen activation is of course key to a wide variety of (electro)chemical reactions. A sentence on some of the most technologically important applications and some additional discussion on the importance of CO CO_2 *in particular would help highlight the importance of this work.*

Response: Thank you for your suggestion. In the introduction, we added the discussion on the importance of CO → CO_2 to highlight the significance of this work as follows. ***"Molecular oxygen activation, a continuous process of adsorption and***

dissociation of O_2 on the catalyst surface (Figure S1), is a key step in catalytic reactions [Chem. Rev., 118, 2816-2862 (2018)], including the synthesis of organic compounds, catalytic combustion of volatile organic compounds (VOCs), oxygen reduction reaction (ORR) in fuel cells and so on [J. Am. Chem. Soc. 134, 13018-13026 (2012); ACS Catal. 11, 6614-6625 (2021); Nat. Catal. 4, 463-468 (2021)].”

“High-efficiency CO oxidation is of great significance in automotive exhaust purification and the anti-toxicity improvement of proton exchange membrane fuel cells [Science 358, 1419–1423 (2017); ACS Catal., 10, 6532−6545 (2020)].”

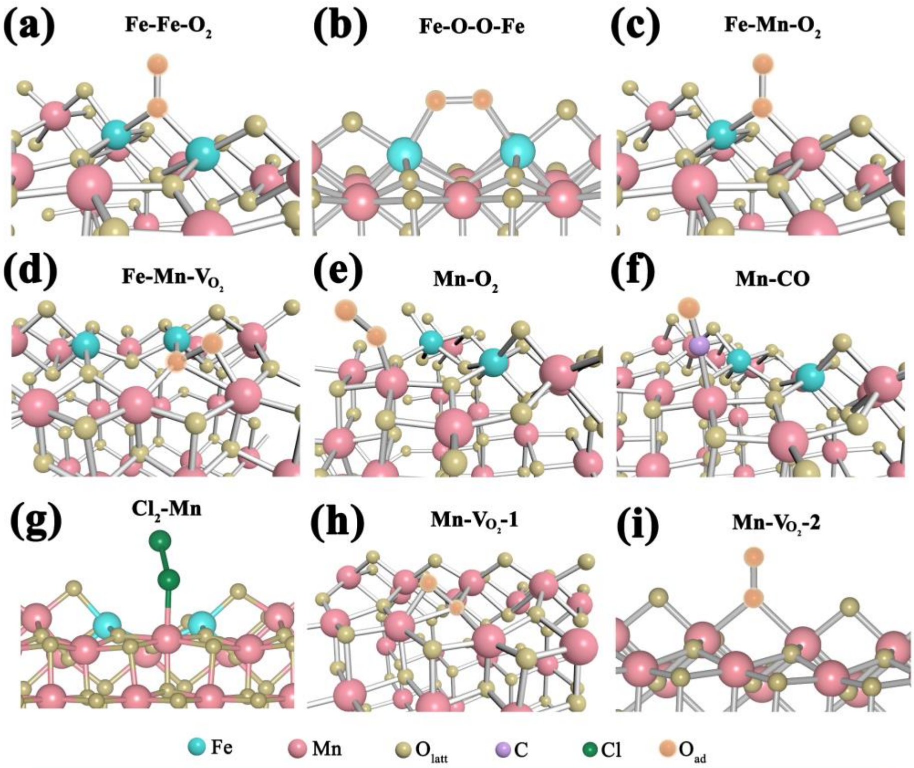
During the revision, more discussion about oxygen activation was added on page 2 and 5 in the revised manuscript and the related Refs. 1-4, 16 and 17 were cited.

3) On a technical level, the denticity/binding motif of the bound O_2 as brought up on page 7 and Figure S10 could be strengthened somewhat. In particular, it seems odd to not have considered and reported on the energetics of the O_2 with 1 O bonded to each of the Fe atoms, even if it is indeed higher energy than the O_2 bridging the 2 Fe with a single O. Also, based on equation 5, it appears that binding does not include vibrational contributions to the free energy including zero-point energies. Given how close some of the competing binding sites are for the O_2, these effects may well shift binding energetics, especially for different binding motifs which should be addressed.

Response: We appreciate the insightful comments from the reviewer. During the revision, we calculated the situation for each oxygen atom from O_2 attached to Fe site (side-on configuration) (Figure R5b), and found that the adsorption energy (-1.47 eV) of O_2 in side-on configuration was significantly lower than that (-2.00 eV) of the end-on adsorption configuration (Fe(O=O)Fe) (Figure R5a). Thereby, the adsorption of O_2 on Fe sites preferred to the end-on mode. Meanwhile, we also calculated the Bader charge and the differential charge density of side-on configuration (Figure R19), and found that two oxygen atoms got the same number of electrons, and the electron density was evenly distributed among the adsorbed oxygen molecule. Therefore, the dipole moment of oxygen molecules did not change during the vibration process, inconsistent with the results of the in-situ DRIFTS. As a result, the adsorption configuration of oxygen on Fe sites in side-on mode was further excluded.

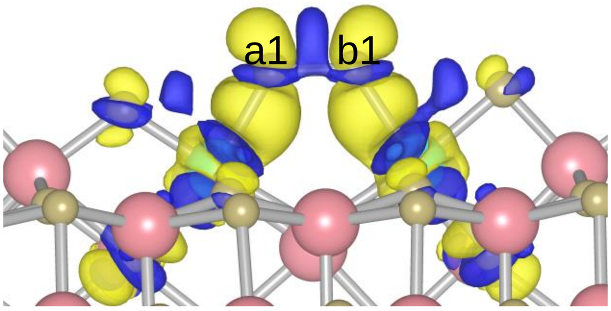
Zero-point energy correction (Table R2) was carried out for each adsorption configuration, and the corresponding adsorption energies was recalculated (Figure R5).

During the revision, Figure R19 and Table R2 was added as the new Supplementary Figure S17 and Table S8, respectively.



Configuration	a	b	c	d	e	f	g	h	i
Adsorption Energy (eV)	-2.00	-1.47	-1.82	-0.83	-1.66	-2.15	-3.11	-2.39	-1.69

Figure R5. The stable configurations of (a-e) O_2, (f) CO and (g) Cl_2 adsorbed at the different sites of Fe/MnO_2 surface, and O_2 adsorbed in (h) the oxygen vacancy or (i) bi-manganese sites of MnO_2. The corresponding adsorption energy with zero-point energy correction is listed in the table of the picture.



Oxygen atom	a1	b1
Bader Charge	-0.12	-0.12

Figure R19. The difference charge density of O_2 adsorbed on Fe/MnO_2. Different oxygen atoms from adsorbed oxygen species were labeled as a1 and b1, and corresponding Bader charge was recorded in the bottom of charge density map. The charge density of yellow and blue represents the concentrated and scarce electrostatic potential scale respectively.

Table R2. Calculated energy and zero-point energy of the corresponding free and adsorbed molecules.

Configuration	**Energy (eV)**	**Zero Point Energy (eV)**	**Corrected Energy (eV)**
Fe-Fe-O_2	-545.52	0.08	-545.44
Fe-O-O-Fe	-544.97	0.06	-544.91
Fe-Mn-O_2	-545.25	0.07	-545.18
Fe-Mn-VO_2	-547.20	0.05	-547.15
Mn-O_2	-545.19	0.09	-545.10
Mn-CO	-551.88	0.12	-551.76
Mn-VO_2-1	-548.80	0.05	-548.75
Mn-VO_2-2	-548.13	0.08	-548.05
Cl_2-Mn	-540.66	0.01	-540.65
O_2	-8.84	0.10	-8.74
CO	-14.80	0.13	-14.67
Cl_2	-3.58	0.03	-3.55

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REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have provided more experimental evidence and calculation results to address my previous concerns, and have revised the manuscript and its SI accordingly. The whole manuscript has been improved drastically. Therefore, I would endorse its acceptance.

Reviewer #2 (Remarks to the Author):

The authors made very good effort for revising manuscript. The results structural characterizations provided in the revised manuscript and supporting information are satisfactory and I'm convinced by the authors' explanation. My one last suggestion is to include the information regarding specific activity at T50 in addition to the activation energies reported already in the manuscript since the mass of Fe is now clear through this revision thanks to the authors' effort for identifying the amount of Fe atoms on MnO2, and discuss it with reported values (see for example, https://www.nature.com/articles/s41929-019-0282-y which summarizes the specific activities of single and few atom catalysts). I consider that the specific activity is one of the important figure of merit of catalyst to consider the practical applications.

Reviewer #3 (Remarks to the Author):

I will defer to the other reviewers on their comments, though they have made some very good points regarding the experimental data and its interpretation. I very much appreciate the authors' work to address the Reviewer 3 comments but I still have some reservations regarding the work as presented though these are fairly minor and should be easily addressed. First, the new term "adjacent single-atom iron" is still somewhat problematic. MnO2-hosted Fe dimer seems like a much more appropriate term given that in the pathways presented, both iron atoms play some direct role, making the "single-atom" phrase inappropriate. I don't understand the continued inclusion in this manuscript. It also looks from the figures that the Fe is integrated into the MnO2 oxide which means these are likely substitutional defects and not adatom like structures. This needs to be made more explicitly clear since "adjacent Fe atoms anchored on MnO2" sounds like dimer pairs of adatoms which does not appear to be the structures considered since oxygen atoms are above the Fe (e.g., Figs. R19 and R5).

Also, more detail is required on the zero-point energy correction (e.g., in what limit was it calculated/ methodology used and which atoms were utilized for calculating… likely only the adsorbing molecule based on values but this should be explicitly stated). The treatment of end-on vs. side-on is appropriate, showing relevant DFT values and the additional DRIFTS argument regarding dipole makes some sense, though having a complimentary end-on O2 plot analogous to R19 would be beneficial for showing there is a dipole shift in such cases, strengthening the dipole argument.

Response Letter

We thank all three Reviewers for their positive reviews and the constructive suggestions that help to improve the scientific presentation of this manuscript. Point-by-Point responses to address the concerns raised by the Reviewers are shown below:

Reviewer #1 (Remarks to the Author):

The authors have provided more experimental evidence and calculation results to address my previous concerns, and have revised the manuscript and its SI accordingly. The whole manuscript has been improved drastically. Therefore, I would endorse its acceptance.

Response: We sincerely thank the Reviewer for the approval of this manuscript.

Reviewer #2 (Remarks to the Author):

The authors made very good effort for revising manuscript. The results structural characterizations provided in the revised manuscript and supporting information are satisfactory and I'm convinced by the authors' explanation. My one last suggestion is to include the information regarding specific activity at T50 in addition to the activation energies reported already in the manuscript since the mass of Fe is now clear through this revision thanks to the authors' effort for identifying the amount of Fe atoms on MnO_2*, and discuss it with reported values (see for example, https://www.nature.com/articles/s41929-019-0282-y, which summarizes the specific activities of single and few atom catalysts). I consider that the specific activity is one of the important figure of merit of catalyst to consider the practical applications.*

Response: Thank you for your nice comment and helpful suggestion. Referring to the remarkable article [*Nat. Catal.*, 2019, 2, 590–602], we calculated the specific activity (R_{T50}) of 0.25% Fe/MnO_2 according to the calculation formula (1) and the value was 310 mol_{CO} h^{-1} mol_{Fe}^{-1} with T50 at 47 °C, higher than those of most platinum group metal (PGM) catalysts.

Specific activity was calculated by the following equation:

$$R_{T50} = \frac{\upsilon_{CO} \times M_{Fe}}{m_{Fe}} \qquad (1)$$

Where υ_{CO} represents the molar gas flow rate of CO (mol/h); M_{Fe} is the relative atomic mass of Fe; m_{Fe} is the mass of Fe on the basis of ICP results and statistical results from 0.25% Fe/MnO_2 STEM image.

During the revision, we also cited this relevant literature [Nat. Catal., 2019, 2, 590–602] as Ref. 18 and added the corresponding discussion on page 20 in the revised manuscript as follows. ***"Simultaneously, we calculated the specific activity (R_{T50}) of 0.25% Fe/MnO_2 according to the calculation formula (10) and the value was 310 mol_{CO} h^{-1} mol_{Fe}^{-1} with T50 at 47 °C, higher than those of most platinum group metal (PGM) catalysts.[18]"***

Reviewer #3 (Remarks to the Author):

I will defer to the other reviewers on their comments, though they have made some very good points regarding the experimental data and its interpretation. I very much appreciate the authors' work to address the Reviewer 3 comments but I still have some reservations regarding the work as presented though these are fairly minor and should be easily addressed. First, the new term "adjacent single-atom iron" is still somewhat problematic. MnO_2-hosted Fe dimer seems like a much more appropriate term given that in the pathways presented, both iron atoms play some direct role, making the "single-atom" phrase inappropriate. I don't understand the continued inclusion in this manuscript. It also looks from the figures that the Fe is integrated into the MnO_2 oxide which means these are likely substitutional defects and not adatom like structures. This needs to be made more explicitly clear since "adjacent Fe atoms anchored on MnO_2" sounds like dimer pairs of adatoms which does not *appear to be the structures considered since oxygen atoms are above the Fe (e.g., Figs. R19 and R5).*

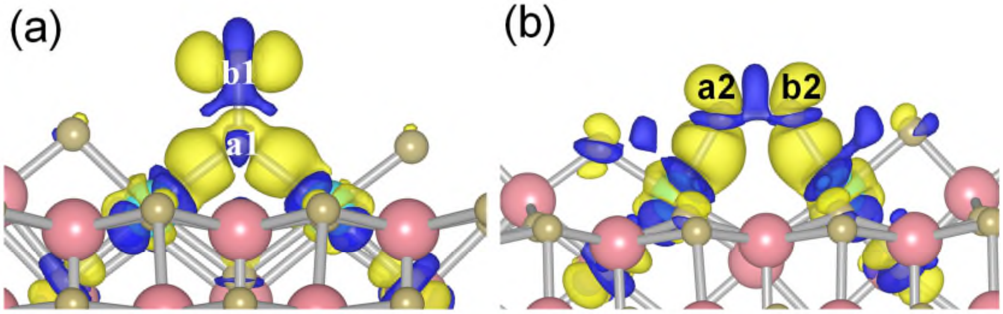
Also, more detail is required on the zero-point energy correction (e.g., in what limit was it calculated/ methodology used and which atoms were utilized for calculating… likely only the adsorbing molecule based on values but this should be explicitly stated). The treatment of end-on vs. side-on is appropriate, showing relevant DFT values and the additional DRIFTS argument regarding dipole makes some sense, though having a complimentary end-on O_2 plot analogous to R19 would be beneficial for showing there is a dipole shift in such cases, strengthening the dipole argument.

Response: We thank the reviewer for the constructive advices and would like to reply to the comments as follows.

(1) In order to avoid the confusion, we added ***"also called as MnO_2-hosted Fe dimer,"*** in the abstract to further explain the structure of catalyst developed in this study.

(2) Zero-point energy correction was obtained from vibrational frequencies by applying normal-mode analysis through density functional theory calculations [*J. Am. Chem. Soc.* 2021, 143, 1399-1408]. We fixed the catalyst substrate and only allowed the adsorbing molecule to vibrate.

(3) We added the configuration of oxygen molecule adsorbed on the two adjacent Fe sites with end-on mode, and Bader charge calculation results revealed the two oxygen atoms had different charges (-0.37 and -0.06) (Figure R1a). The different charges constantly changed the dipole moment of O_2 in the vibration process, accounting for the infrared characteristic absorption peak of Fe(O=O)Fe. However, for the side-on configuration (Figure R1b), two oxygen atoms got the same number of electrons, and the electron density was evenly distributed among the adsorbed oxygen molecule. Therefore, the dipole moment of oxygen molecules did not change during the vibration process. As a result, the adsorption configuration of oxygen on Fe sites was determined with end-on mode.



Fe/MnO_2	**End-on**		**Side-on**	
	a1	b1	a2	b2
Bader Charge	-0.37	-0.06	-0.12	-0.12

Figure R1. The difference charge density of O_2 adsorbed on Fe/MnO_2 with (a) end-on and (b) side-on mode. Different oxygen atoms from adsorbed oxygen species were labeled as a and b, and corresponding Bader charge was recorded in the bottom of charge density map. The charge density of yellow and blue represents the concentrated and scarce electrostatic potential scale respectively.

During the revision, Figure R1 was added as the Figure 3d and the Supplementary Figure S18. The discussion about zero-point energy correction was added on page 6 in the revised manuscript as follows. ***"Zero-point energy correction was obtained from vibrational frequencies by applying normal-mode analysis through density functional theory calculations.[43] We fixed the catalyst substrate and only allowed the adsorbing molecule to vibrate."***

References cited in the Response Letter.

[1] Beniya, A. & Higashi, S. Towards dense single-atom catalysts for future automotive applications. *Nat. Catal.* **2**, 590-602 (2019).

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