Reviewer #1 (Remarks to the Author):

This manuscript is an interesting contribution to efforts aimed at controlling catalyst selectivity with organic modifiers. Here, the authors have used a novel type of modification, employing carboxylic acids to MnOx catalysts. They find that the carboxylic acids block sites associated with reaction of hydroxyl groups, allowing preservation of those groups during ammoxidation reactions. The authors demonstrate the basic mechanism for suppression of hydroxyl reaction via a nice set of infrared spectroscopy experiments. Overall, I think the manuscript is publishable in Nature Communications, though I do have a few suggestions for the manuscript:

(1) Probably the most significant issue with the manuscript was that reaction kinetics weren’t really reported in much detail, but instead the authors report conversions (as in Figure 5). While it is certainly important that the modified catalysts can achieve high selectivity at nearly full conversion, it would be useful to know how the modifiers affect the rate constants for the reactions. This is of practical importance, but also would provide additional insights on the catalysis. For example, does the rate of the desired reaction actually increase for the modified catalyst, or is it simply a case of selective poisoning?

(2) I am not expert in manganese oxide surface chemistry, but I found it somewhat surprising that monodentate carboxylic acid adsorption was favored at low coverage, while the bidentate structure became populated at high coverage. Intuitively, I would expect the opposite trend, where the less crowded surface allows for more points of coordination with the acid. Is there any precedent for the trend proposed by the authors on related metal oxides? If not, are there other possible interpretations of these spectra?

(3) Have the authors attempted to recycle their material, or conducted experiments in such a way that it can be clearly demonstrated that the catalyst performance remains steady over time? Figure 7 seems to be aimed at this, but it wasn’t clear to me that it showed negligible loss of activity during operation. One might expect carboxylates to become detached under reaction conditions, or to undergo some form of degradation.

(4) Do the authors have a suggestion for why the carboxylic acids selectively poison reactions of the hydroxyl, but do not poison the desired ammoxidations?

(5) The data in general (as in Figure 5 and Table 1) do not include estimates of uncertainties; can these be provided?

(6) Minor point: the authors rightly point out that there have been few studies using organic modifiers on metal oxides, but there is one very recent publication on modification of TiO2 for
selectivity enhancement: http://dx.doi.org/10.1021/acscatal.7b02789

(7) The English is comprehensible, but there are numerous places where there are grammatical mistakes. In addition, in one case “metal” was misspelled as “meal”.

**Reviewer #2 (Remarks to the Author):**

The manuscript is dealing with the selective ammoxidation of 4-hydroxymethyl benzaldehyde and 5-hydroxymethyl furfural using MnOx modified with carboxylic acids. Here, it is very important to suppress the oxidation of OH group, and the strategy of the catalyst design is the poisoning of the oxidation site with the adsorption of carboxylic acids.

The present work may include interesting results, however, the demonstration is not appropriate. At first, authors should show the potential of MnOx without modification. For example, authors should show the results of MnOx at lower reaction temperature because the activity of MnOx is much higher than carboxylic acid-modified catalysts. At the same time, authors had better show the results of the activity test below 100% conversion. In particular, the activity of MnOx without and with the modification was so different, and the selectivity should not discussed from the data around 100%. Authors should show the highest yield obtained on MnOx without modification by adjusting the reaction conditions such as reaction temperature, and reaction time, the ratio of the substrate to catalyst.

Another important point is the low activity of MnOx modified with carboxylic acids. Under the present reaction conditions, the turnover number per total Mn amount is calculated to be about only 3. Authors should demonstrate the data of much higher TON because it is very easy using much higher ratio of the substrate to catalyst, or reusability of the catalyst. In particular, in the present work, the catalyst stability and reusability should be demonstrate.

Moreover, authors should determine the amount of the adsrobed carboxylic acid during the reaction. Authors used the excess of carboxylic acids. How large is the amount of carboxylic acid in the solution? The amount of the adsorbed carboxylic acid may be influenced by the presence of NH3 in the reaction system, and so on.

At present, it is very difficult to recommend for the publication.

**Reviewer #3 (Remarks to the Author):**

This paper is very poorly written. There are problems with grammar, words that make no sense, and other significant problems with the use of English. The paper needs to be rewritten by someone who knows the science of the work and English. In addition, there are scientific issues. Benzyl alcohol oxidation is easy to drive. The data are all > 99% conversion signifying equilibrium not catalysis. Figure 5 needs error bars on all data points. Figure 7 needs error bars
on all data points. If the product is chiral then either the surface or the reactant need to be chiral. This does not appear to the case.
Referee: 1

This manuscript is an interesting contribution to efforts aimed at controlling catalyst selectivity with organic modifiers. Here, the authors have used a novel type of modification, employing carboxylic acids to MnO$_x$ catalysts. They find that the carboxylic acids block sites associated with reaction of hydroxyl groups, allowing preservation of those groups during ammoxidation reactions. The authors demonstrate the basic mechanism for suppression of hydroxyl reaction via a nice set of infrared spectroscopy experiments. Overall, I think the manuscript is publishable in Nature Communications, though I do have a few suggestions for the manuscript:

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Response: Thank you for the reviewer’s comments and nice suggestions. While it is significant to achieve high selectivity at nearly full conversion, the reaction kinetics should be investigated to provide insights on the ammoxidation activity of unmodified and modified catalyst. Aerobic oxidation reaction over manganese oxide catalyst is a complex cascade reaction without simple order; therefore we were not successful in predicting the rate constant. Instead, the time course of ammoxidation of 4-hydroxymethylbenzaldehyde on MnO$_x$ and HAc modified MnO$_x$ has been studied, respectively. As shown in Fig. R1a, the initial stage of reaction gave comparable amount of hydroxynitrite and dinitrile on unmodified MnO$_x$. By contrast, dinitrile was not detected on HAc modified MnO$_x$ (Fig. R1b, Fig. R1d), indicating an extremely low rate of dinitrile formation. However, the rate of hydroxynitrite production was slightly decreased after modification (Fig. R1c). Thus, the enhanced chemoselectivity was not because of an increase in the rate of the desired reaction but rather a result of
inhibition of the undesired reaction for the modified catalyst.

**Fig. R1** (Fig. 7 in the manuscript) Time course of aerobic ammoxidation of 4-hydroxymethylbenzaldehyde. **a** MnO\(_x\) as catalyst. **b** HAc modified MnO\(_x\) as catalyst. **c** Time course of 2 formation over MnO\(_x\) and HAc modified MnO\(_x\), respectively. **d** Time course of 3 formation over MnO\(_x\) and HAc modified MnO\(_x\), respectively. Reaction conditions: 0.5 mmol 4-hydroxymethyl-benzaldehyde, 0.17 mmol MnO\(_x\), HAc/MnO\(_x\) = 120 mol% for HAc modified MnO\(_x\), 5 mL CH\(_3\)CN, 0.3 MPa NH\(_3\), 0.3 MPa O\(_2\), 80 °C.

**Comment 2:** I am not expert in manganese oxide surface chemistry, but I found it somewhat surprising that monodentate carboxylic acid adsorption was favored at low coverage, while the bidentate structure became populated at high coverage. Intuitively, I would expect the opposite trend, where the less crowded surface allows for more points of coordination with the acid. Is there any precedent for the trend proposed by the authors on related metal oxides? If not, are there other possible interpretations of these spectra?

**Response:** It was previously reported that the adsorption of carboxylate on TiO\(_2\) as bridging and monodentate binding modes are both energetically quite favorable, with small difference in adsorption energies: the bridging mode is typically about 10-25 kJ/mol more stable (Lars Ojamäe, et al., Journal of colloid and interface science, 2006, 296(1): 71-78). Nevertheless, carboxylate preferentially binds to the highly coordinative unsaturated sites on metal oxides through a single metal-O bond with
high strength, resulting in kinetically favored monodentate configuration; and due to
the presence of the H-bond between the surface metal-OH and the O of the
carboxylate binding to the metal, rotation of carboxylate or transformation to other
mode is hindered (Gong, Xueqing, et al., Journal of Physical Chemistry B, 2006,
110(6): 2804-2811). Herein, highly coordinative unsaturated sites should be available
at low coverage for kinetically favored monodentate mode adsorption on MnOx.

**Comment 3:** Have the authors attempted to recycle their material, or conducted
experiments in such a way that it can be clearly demonstrated that the catalyst
performance remains steady over time? Figure 7 seems to be aimed at this, but it
wasn’t clear to me that it showed negligible loss of activity during operation. One
might expect carboxylates to become detached under reaction conditions, or to
undergo some form of degradation.

**Response:** We attempted to extend the reaction time to 18 h, and found that the
selectivity for hydroxynitrile was well preserved with just slight decrease (Fig. R2).
The capability of preventing alcohol ammoxidation over a long period suggests that
the regulated chemisorption properties on the carboxylate modified catalyst surface
cannot be easily destroyed under the reaction conditions. Moreover, the catalyst can
be recycled without selectivity loss by regeneration (Fig. R3).

![Conversion and Selectivity](image.png)

**Fig. R2** (Fig. 8 in the manuscript) Time course of catalytic conversion of
4-hydroxymethylbenzaldehyde to 4-cyanobenzyl alcohol over HAc modified MnOx. Reaction
conditions: 2.5 mmol 4-hydroxymethyl-benzaldehyde, 0.85 mmol MnOx, HAc/MnOx = 300 mol%,
25 mL CH3CN, 0.3 MPa NH3, 0.3 MPa O2, 80 °C.
Recyclability test results for selective ammoxidation of 4-hydroxymethylbenzaldehyde catalyzed by HAc modified MnOx. Reaction conditions: 0.5 mmol 4-hydroxymethyl-benzaldehyde, 0.17 mmol MnOx, HAc/MnOx = 120 mol%, 5 mL CH3CN, 0.3 MPa NH3, 0.3 MPa O2, 80 °C, 3 h. At the completion of the reaction, the solution was separated by centrifugation and analyzed by GC using the internal standard method. The catalyst was washed with CH3CN 3 times and then regenerated by adding HAc (HAc/MnOx = 120 mol%) to the reaction mixture for the cycle experiments.

Comment 4: Do the authors have a suggestion for why the carboxylic acids selectively poison reactions of the hydroxyl, but do not poison the desired ammoxidations?

CH3OH adsorption FT-IR spectra of unmodified and HAc-modified manganese oxides.

Response: To examine the effect of carboxylic acid modification on the
chemisorption behavior of alcohol on manganese oxide, in situ CH$_3$OH adsorption Fourier transform infrared spectroscopy (FT-IR) characterization (Fig. R4) was investigated. Methanol is dissociated into methoxy species on unmodified MnO$_x$ and the bands of methoxy species at 1090 and 1028 cm$^{-1}$ assigned to the ν(C-O) were observed. Under equivalent conditions, the C-O vibrations arising from methoxy species were barely observed over HAc-modified MnO$_x$. The above results indicated that carboxylic acid can occupy the adsorptive sites for alcohol and the high stability of carboxylate adsorption hindered the potential replacement by alcohol. The higher adsorption stability of carboxylic acid compared with alcohol on metal oxides was also confirmed by density functional theory study (Gong, Xueqing, et al., Journal of Physical Chemistry B, 2006, 110(6): 2804–2811). In this way, the carboxylic acid modification poisoned the reaction of hydroxyl group. The aldehyde ammoxidation was not obviously affected, possibly because of the much different activation manner of C=O in aldehyde and C≡NH in aldimine intermediate on metal oxides in comparison with alcohol.

**Comment 5:** The data in general (as in Figure 5 and Table 1) do not include estimates of uncertainties; can these be provided?

![Fig. R5](image-url) **Fig. R5** (Fig. 5 in the manuscript) Performance of manganese oxides with different modifiers in ammoxidation of 4-hydroxymethylbenzaldehyde. Reaction conditions: 0.5 mmol 4-hydroxymethylbenzaldehyde, 0.17 mmol MnO$_x$, additive/MnO$_x$ = 120 mol%, 5 mL CH$_3$CN, 0.3 MPa NH$_3$, 0.3 MPa O$_2$, 80 °C, 3 h.
Table R1 (Table 1 in the manuscript). Performance of manganese oxides with different amount of HAc modifiers in ammoxidation of 4-hydroxymethylbenzaldehyde. a

| Entry | HAc/MnO₂ (mol%) | Conv. (%) | Select. (%) |
|-------|-----------------|-----------|-------------|
| 1b    | 0               | > 99      | 0           | 81 ± 1      |
| 2     | 6               | > 99      | 12 ± 3      | 66 ± 1      |
| 3     | 12              | > 99      | 45 ± 1      | 41 ± 3      |
| 4     | 30              | > 99      | 71 ± 2      | 25 ± 2      |
| 5     | 120             | > 99      | 91 ± 1      | 2 ± 1       |
| 6     | 300             | > 99      | 92 ± 1      | 1 ± 0.4     |

aReaction conditions: 0.5 mmol 4-hydroxymethyl-benzaldehyde, 0.17 mmol MnO₂, 5 mL CH₃CN, 0.3 MPa NH₃, 0.3 MPa O₂, 80 °C, 3 h. b18 ± 1% 4-Cyanobenzamide was detected.

Response: As shown in Fig. R5, table R1 and Fig. R2 and the revised manuscript, the estimates of uncertainties have been added to the data in Fig. 5, Table 1 and Fig. 8.

Comment 6: Minor point: the authors rightly point out that there have been few studies using organic modifiers on metal oxides, but there is one very recent publication on modification of TiO₂ for selectivity enhancement: http://dx.doi.org/10.1021/acscatal.7b02789

Response: This excellent work on utilization of organic modifiers for controlling the surface reactivity of titania has been added to the reference list.

Comment 7: The English is comprehensible, but there are numerous places where there are grammatical mistakes. In addition, in one case “metal” was misspelled as “meal”.

Response: We are sorry for the mistakes. We corrected the misspelled word. In addition, we improved our written English via “English Language Editing service” provided by Springer Nature.
Referee: 2

The manuscript is dealing with the selective ammoxidation of 4-hydroxymethyl benzaldehyde and 5-hydroxymethyl furfural using MnO\textsubscript{x} modified with carboxylic acids. Here, it is very important to suppress the oxidation of OH group, and the strategy of the catalyst design is the poisoning of the oxidation site with the adsorption of carboxylic acids.

Comment 1: The present work may include interesting results, however, the demonstration is not appropriate. At first, authors should show the potential of MnO\textsubscript{x} without modification. For example, authors should show the results of MnO\textsubscript{x} at lower reaction temperature because the activity of MnO\textsubscript{x} is much higher than carboxylic acid-modified catalysts. At the same time, authors had better show the results of the activity test below 100% conversion. In particular, the activity of MnO\textsubscript{x} without and with the modification was so different, and the selectivity should not discussed from the data around 100%. Authors should show the highest yield obtained on MnO\textsubscript{x} without modification by adjusting the reaction conditions such as reaction temperature, and reaction time, the ratio of the substrate to catalyst.

Response: Thank you for the reviewer’s comments and nice suggestions. The catalytic ammoxidation reaction over MnO\textsubscript{x} has been studied by adjusting the reaction conditions like reaction time (Fig. R6), reaction temperature (Fig. R7) and ratio of the substrate to catalyst (Fig. R8). However, in spite of the reduced reaction time, decreased reaction temperature or decreased amount of catalyst, the chemoselective ammoxidation product was observed at low selectivity. Approximately 30% of the chemoselective hydroxynitrile ammoxidation product was obtained as the highest yield.

Besides the results at 100% conversion, we further studied the catalytic selectivity at 90%, 70% and 50% conversions, respectively, to obtain a better understanding of the role of the carboxylic acid in the ammoxidation reaction catalyzed by MnO\textsubscript{x} (Fig. R9). And a steadily increased selectivity for hydroxynitirle was observed with increasing the carboxylate concentration at 90%, 70% and 50% conversions, respectively. This is in accordance with the change of selectivity at 100%
conversion (Table R1). By the way, a relatively low selectivity at 50% and 70% conversions was observed, which should be attributed to the formation of aldimine intermediate.

The reaction kinetics was also investigated to provide insights on the ammoxidation activity of catalyst. As shown in Fig. R1a, the initial stage of reaction gave comparable amount of hydroxynitirle and dinitrile on unmodified MnO₂. By contrast, dinitrile was not detected on HAc modified MnO₂ (Fig. R1b, Fig. R1d), indicating an extremely low rate of dinitrile formation. However, the rate of hydroxynitirle production was slightly decreased after modification (Fig. R1c). Thus, the enhanced chemoselectivity was not because of an increase in the rate of the desired reaction but rather a result of inhibition of the undesired reaction for the modified catalyst.

**Fig. R6** Time course of aerobic ammoxidation of 4-hydroxymethylbenzaldehyde over MnO₂ at 80 °C. Reaction conditions: 0.5 mmol 4-hydroxymethyl-benzaldehyde, MnO₂/substrate = 34 mol%, 5 mL CH₃CN, 0.3 MPa NH₃, 0.3 MPa O₂, 80 °C.

**Fig. R7** Time course of aerobic ammoxidation of 4-hydroxymethylbenzaldehyde over
\textbf{MnO}_x \textit{at 50 °C}. Reaction conditions: 2.5 mmol 4-hydroxymethyl-benzaldehyde, MnO\textsubscript{x}/substrate = 34 mol\%, 25 mL CH\textsubscript{3}CN, 0.3 MPa NH\textsubscript{3}, 0.3 MPa O\textsubscript{2}, 50 °C.

\textbf{Fig. R8} Time course of aerobic ammoxidation of 4-hydroxymethylbenzaldehyde over MnO\textsubscript{x}. Reaction conditions: 2.5 mmol 4-hydroxymethyl-benzaldehyde, MnO\textsubscript{x}/substrate = 17 mol\%, 25 mL CH\textsubscript{3}CN, 0.3 MPa NH\textsubscript{3}, 0.3 MPa O\textsubscript{2}, 50 °C.

\textbf{Fig. R9} Selectivity toward 4-cyanobenzyl alcohol for the ammoxidation of 4-hydroxymethylbenzaldehyde on MnO\textsubscript{x} as a function of HAc/MnO\textsubscript{x}. Reaction conditions: 2.5 mmol 4-hydroxymethyl-benzaldehyde, MnO\textsubscript{x}/substrate = 34 mol\%, 5 mL CH\textsubscript{3}CN, 0.3 MPa NH\textsubscript{3}, 0.3 MPa O\textsubscript{2}, 80 °C.

\textbf{Comment 2:} Another important point is the low activity of MnO\textsubscript{x} modified with carboxylic acids. Under the present reaction conditions, the turnover number per total Mn amount is calculated to be about only 3. Authors should demonstrate the data of much higher TON because it is very easy using much higher ratio of the substrate to catalyst, or reusability of the catalyst. In particular, in the present work, the catalyst stability and reusability should be demonstrated.

\textbf{Response:} We attempted to recycle the catalyst. As shown in Fig.R3, the catalyst can
be recycled for at least 9 times without selectivity loss by regeneration.

Fig. R3 Recyclability test results for selective ammoxidation of 4-hydroxymethylbenzaldehyde catalyzed by HAc modified MnOₓ. Reaction conditions: 0.5 mmol 4-hydroxymethyl-benzaldehyde, MnOₓ/substrate = 34 mol%, HAc/MnOₓ = 120 mol%, 5 mL CH₃CN, 0.3 MPa NH₃, 0.3 MPa O₂, 80 °C, 3 h. At the completion of the reaction, the solution was separated by centrifugation and analyzed by GC using the internal standard method. The catalyst was washed with CH₃CN 3 times and then regenerated by adding HAc (HAc/MnOₓ = 120 mol%) to the reaction mixture for the cycle experiments.

Comment 3: Moreover, authors should determine the amount of the adsorbed carboxylic acid during the reaction. Authors used the excess of carboxylic acids. How large is the amount of carboxylic acid in the solution? The amount of the adsorbed carboxylic acid may be influenced by the presence of NH₃ in the reaction system, and so on.

Response: Thank you for the reviewer’s comments. It is difficult to measure the amount of the real-time adsorbed carboxylic acid during the reaction. Though, we measured the adsorbing capacity of MnOₓ at 30 °C using n-hexanoic acid as probing molecule considering its similar effect to HAc (Fig. R5) and convenience in analysis by GC. The adsorptive property of carboxylic acid on MnOₓ was investigated at various concentrations (Fig. R10). The result showed that the adsorption of carboxylic acid on MnOₓ was nearly complete in the range of 0-12 mol% of n-hexanoic acid and increased slowly in range above 12 mol% which indicated the excess of unadsorbed carboxylic acids in the solution (Fig. R10).
It is reasonable to expect the reaction of carboxylic acid in the solution with NH$_3$ to form ammonium acetate. Ammonium acetate, which is strong electrolyte, should also have the capacity to release carboxylate to modify the catalyst surface. As shown in Table R2, ammonium acetate showed comparable effect on the MnO$_x$ catalyzed selective ammonoxidation of 4-hydroxymethylbenzaldehyde in comparison with HAc. Thus we can conclude that the reaction of NH$_3$ in the reaction system with carboxylic acid has little effect on the carboxylate adsorption and modification on MnO$_x$.

![Fig. R10 Fig. 4. The chart of the n-hexanoic acid adsorption on MnO$_x$ (30 °C).](image)

| Table R2. Performance of manganese oxides with ammonium acetate modifier in ammonoxidation of 4-hydroxymethylbenzaldehyde.$^a$ |
|---|---|---|---|
| Entry | Modifier | Conv. (%) | Select. (%) |
| 1 | Ammonium acetate | $> 99$ | 86 | 2 |

$^a$Reaction conditions: 0.5 mmol 4-hydroxymethyl-benzaldehyde, 0.17 mmol MnO$_x$, ammonium acetate/MnO$_x = 120$ mol%, 5 mL CH$_3$CN, 0.3 MPa NH$_3$, 0.3 MPa O$_2$, 80 °C, 3 h.
**Referee: 3**

**Comment**: This paper is very poorly written. There are problems with grammar, words that make no sense, and other significant problems with the use of English. The paper needs to be rewritten by someone who knows the science of the work and English. In addition, there are scientific issues. Benzyl alcohol oxidation is easy to drive. The data are all > 99% conversion signifying equilibrium not catalysis. Figure 5 needs error bars on all data points. Figure 7 needs error bars on all data points. If the product is chiral then either the surface or the reactant need to be chiral. This does not appear to the case.

**Response**: Thanks for the reviewer’s comments and suggestions. We improved our written English via “English Language Editing service” provided by Springer Nature. The selectivity under lower conversion has been studied (Fig. R9). A steadily increased selectivity for hydroxynitrile was observed with increasing the carboxylate concentration at 90%, 70% and 50% conversions. This is in accordance with the change of selectivity at 100% conversion (Table R1).

The reaction kinetics was also investigated to provide insights on the ammoxidation activity of catalyst. As shown in Fig. R1a, the initial stage of reaction gave comparable amount of hydroxynitrile and dinitrile on unmodified MnO₅. By contrast, dinitrile was not detected on HAc modified MnO₅ (Fig. R1b, Fig. R1d), indicating an extremely low rate of dinitrile formation. However, the rate of hydroxynitrile production was slightly decreased after modification (Fig. R1c). Thus, the enhanced chemoselectivity was not because of an increase in the rate of the desired reaction but rather a result of inhibition of the undesired reaction for the modified catalyst.

In addition, as shown in Fig. R2 and Fig. R5, we added error bars after repeat measurements. Organic modification with chiral modifiers is a powerful tool to enhance the chiral selectivity. While, herein the ammoxidation product is not chiral. Controlling chiral selectivity in ammoxidation reaction is potentially significant work, which deserves study in the future.
Fig. R9 Selectivity toward 4-cyanobenzyl alcohol for the ammoxidation of 4-hydroxymethylbenzaldehyde on MnO$_x$ as a function of HAc/MnO$_x$. Reaction conditions: 2.5 mmol 4-hydroxymethyl-benzaldehyde, MnO$_x$/substrate = 34 mol%, 5 mL CH$_3$CN, 0.3 MPa NH$_3$, 0.3 MPa O$_2$, 80 °C.

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Fig. R5 (Fig. 5 in the manuscript) Performance of manganese oxides with different modifiers in ammoxidation of 4-hydroxymethylbenzaldehyde. Reaction conditions: 0.5 mmol 4-hydroxymethylbenzaldehyde, 0.17 mmol MnOₓ, additive/MnOₓ = 120 mol%, 5 mL CH₃CN, 0.3 MPa NH₃, 0.3 MPa O₂, 80 °C, 3 h.
Reviewers’ comments:

Reviewer #1 (Remarks to the Author):

I think the authors have done a good job of responding to the reviews, and their paper is now publishable in Nature Communications.

Reviewer #2 (Remarks to the Author):

The manuscript was revised appropriately.

Reviewer #3 (Remarks to the Author):

Some of the suggestions have been followed including a rewrite of the paper. There are new kinetic data as well.