Supporting Information

Effect and Mechanism of Aluminum(III) for Guaiacol-Glyoxylic acid Condensation Reaction in Vanillin Production

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Experiment Section:

The influence factor optimizes for the condensation conditions:

1 The influence of pH value for the reaction

2 The influence of molar ratio of guaiacol and glyoxylic acid for the reaction

3 The influence of reaction time for the reaction

4 The influence of reaction temperature for the reaction

1. The influence of pH value for the reaction

It has been previously demonstrated that the pH of the reaction solution is crucial to inhibit the disproportionation reaction of glyoxylic acid. Therefore, the effect of pH on product selectivity was first studied at room temperature (20 ^{o}C), reaction time of 40 h and the molar ratio of guaiacol to glyoxylic acid of 1.2:1. The optimum conditions were determined as pH=11.5 by comprehensive raw material conversion and product selectivity.

2. The influence of molar ratio of guaiacol and glyoxylic acid for the reaction

Different molar ratio of guaiacol to glyoxylic acid will lead to different product selectivity. When the molar ratio of glyoxylic acid is greater than that of guaiacol, the selectivity of di-VMA will be the greatest. Therefore, the effect of molar ratio on the selectivity of target product was explored at room temperature (20 ^{o}C), pH=11.5, reaction time of 40 h. Finally, the molar ratio of guaiacol to glyoxylic acid of 1.3:1 was determined to be the optimal reaction condition.

3. The influence of reaction time for the reaction

In order to ensure the maximization of guaiacol conversion and minimize the production of by-product, the effect of reaction time on product selectivity was studied at room temperature, pH=11.5, and the molar ratio of guaiacol to glyoxylic acid was 1.3:1. The results showed that 20-26 h was the most favorable for the reaction time.

4. The influence of reaction temperature for the reaction

For the effect of different temperatures on product selectivity, at pH=11.5, the molar ratio of guaiacol to glyoxylic acid was 1.3:1, and the reaction time of 24 h. It was found that too high temperature was not conducive to the improvement of VMA selectivity, so the optimal reaction temperature was determined at 20 ^{o}C.

Figure S1. The effect of pH value for guaiacol conversion.

Figure S2. The effect of material mole ratio for guaiacol conversion.

Figure S3. The effect of reaction time for guaiacol conversion.

Figure S4. The effect of reaction temperature for guaiacol conversion.

Figure S5. Comparison of catalytic effect of Al^{3+} under different recycle times.

Figure S6. The effect of $Al(NO_3)_3$ and $AlCl_3$ for the selectivity of target products.

Figure S7. The effect of reaction temperature for the selectivity of target products with the present of Al^{3+}.

Figure S8. The effect of adding Al^{3+} on the condensation reaction of guaiacol with formaldehyde.

Figure S9. The effect of adding Zn^{2+} on product selectivity.

Figure S10. (a) The *in-situ* FT-IR spectra of ZnGO, (b) Coordination mode of Zn^{2+} with guaiacol.

Figure S11. The changes of glyoxylic acid conversion following time.

Figure S1.

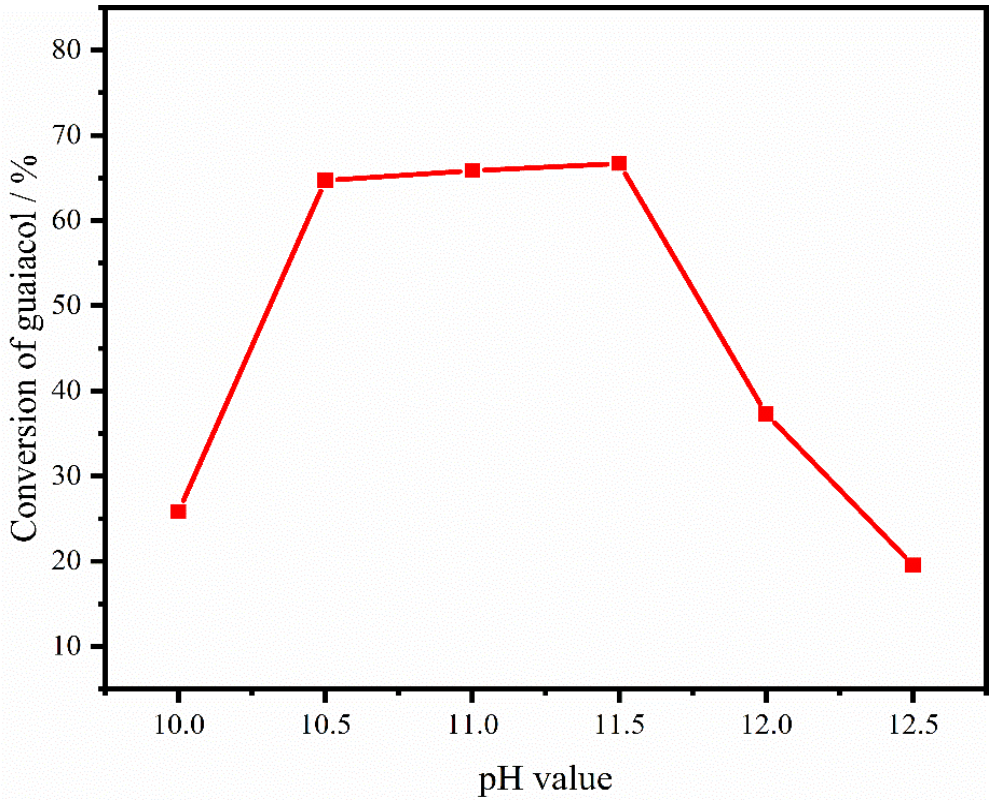

Conversion of guaiacol / %
80
70
60
50
40
30
20
10
10.0
10.5
11.0
11.5
12.0
12.5
pH value

Figure S2.

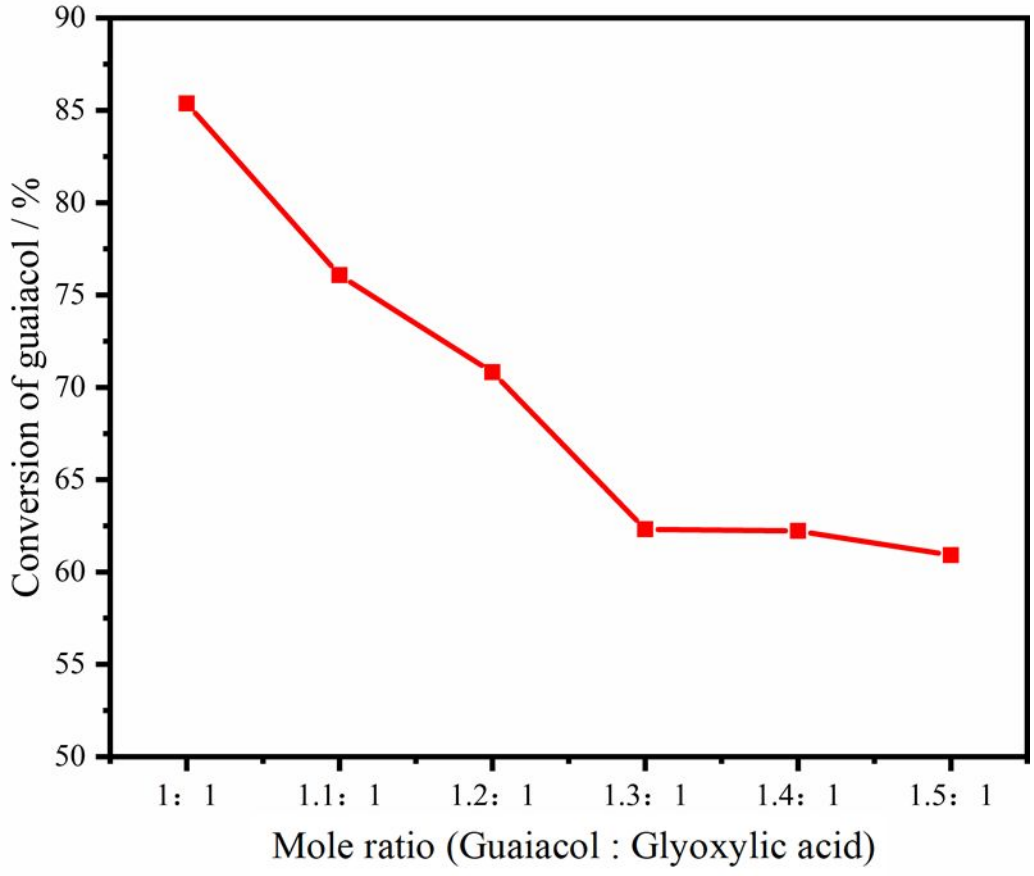

90
85
80
75
70
65
60
55
50
Conversion of guaiacol / %
1：1
1.1：1
1.2：1
1.3：1
1.4：1
1.5：1
Mole ratio (Guaiacol : Glyoxylic acid)

Figure S3.

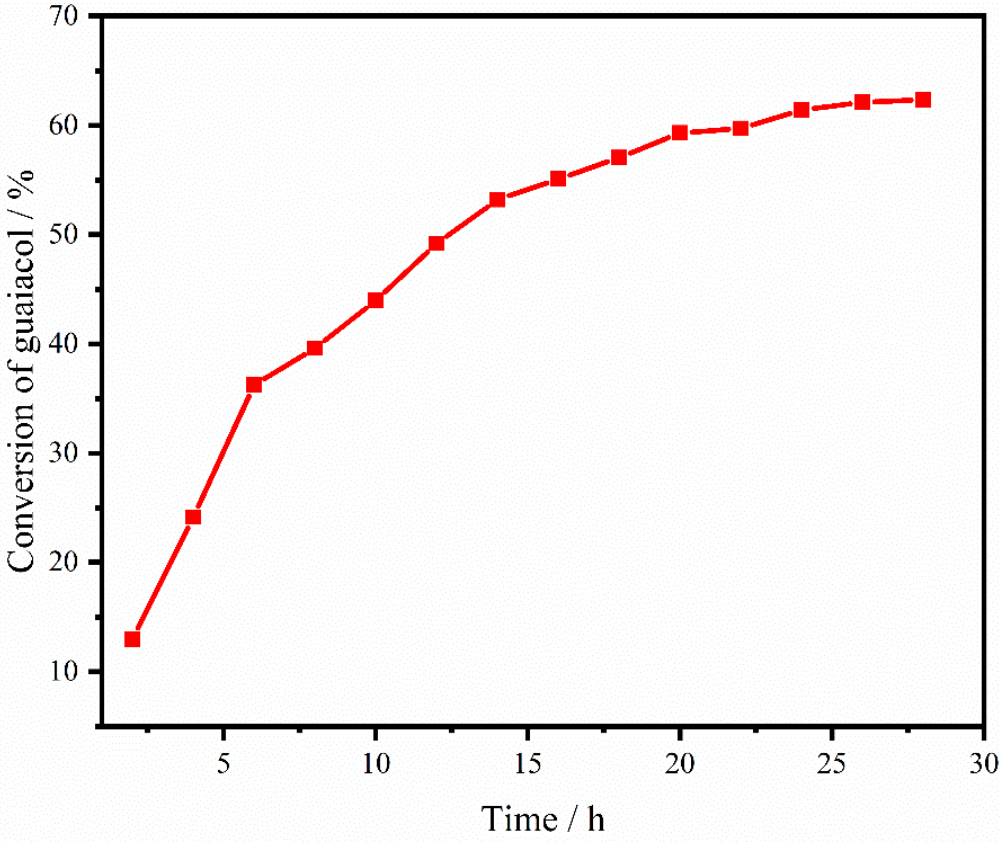

Conversion of guaiacol / %
70
60
50
40
30
20
10
5
10
15
20
25
30
Time / h

Figure S4.

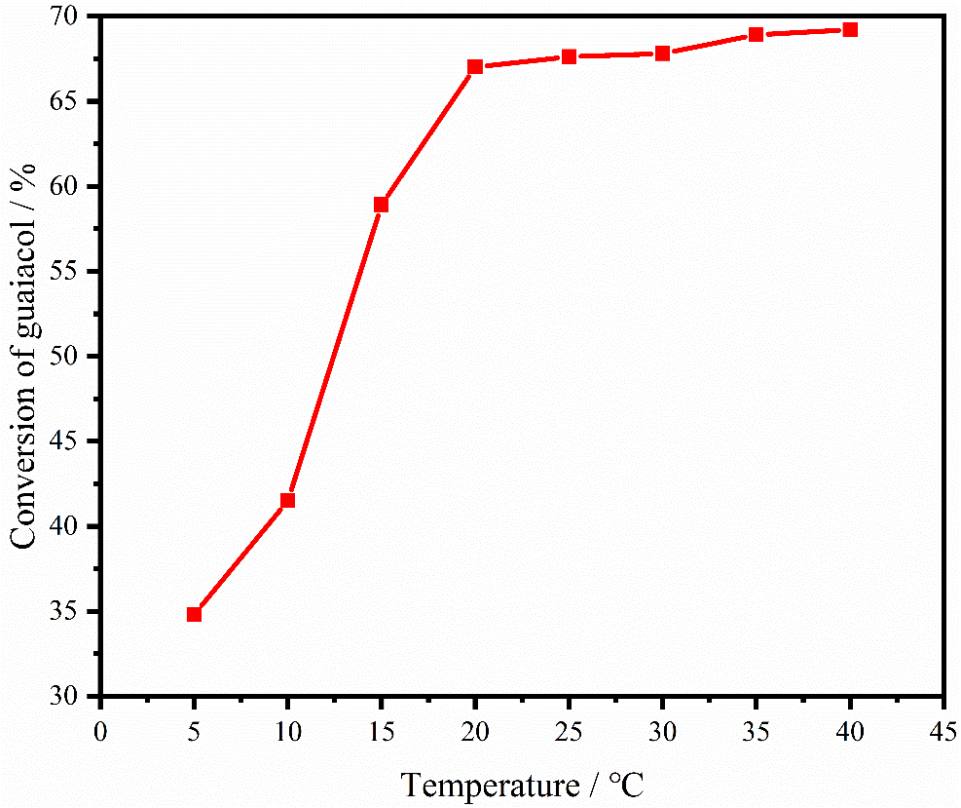

Conversion of guaiacol / %
70
65
60
55
50
45
40
35
30
0
5
10
15
20
25
30
35
40
45
Temperature / °C

Figure S5.

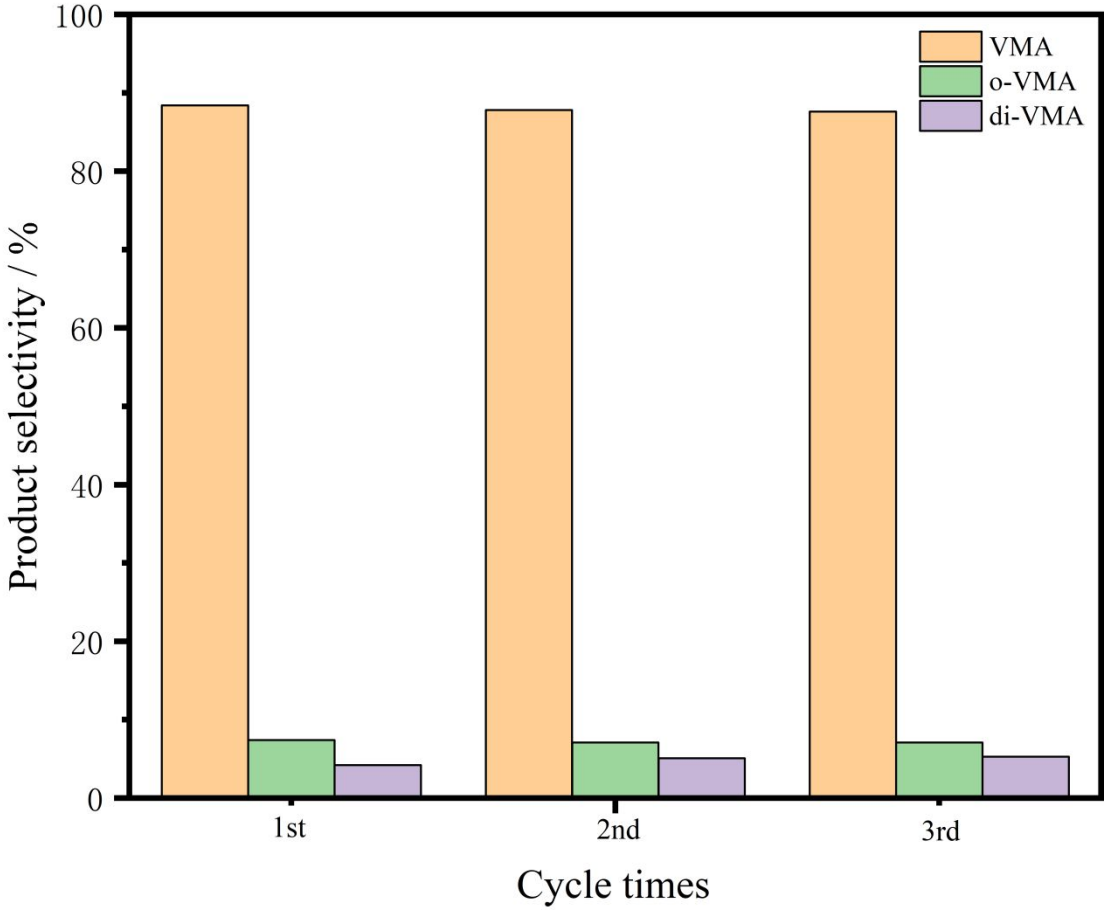

100
80
60
40
20
0
Product selectivity / %
VMA
o-VMA
di-VMA
1st
2nd
3rd
Cycle times

Figure S6.

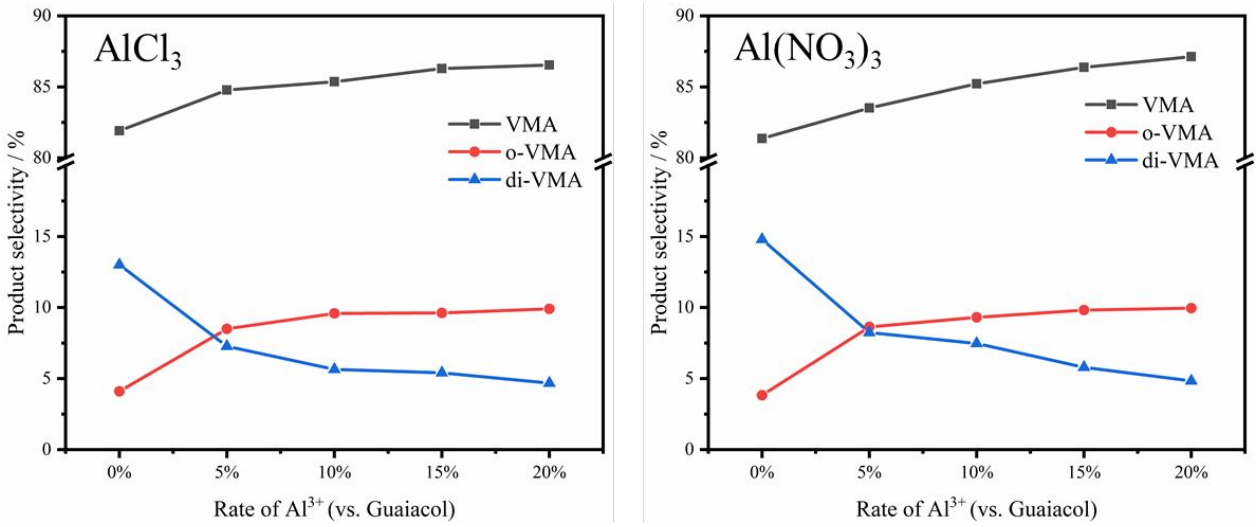

AlCl3
Al(NO3)3
VMA
o-VMA
di-VMA
Product selectivity / %
Rate of Al3+ (vs. Guaiacol)
0%
5%
10%
15%
20%
0
5
10
15
80
85
90

Figure S7.

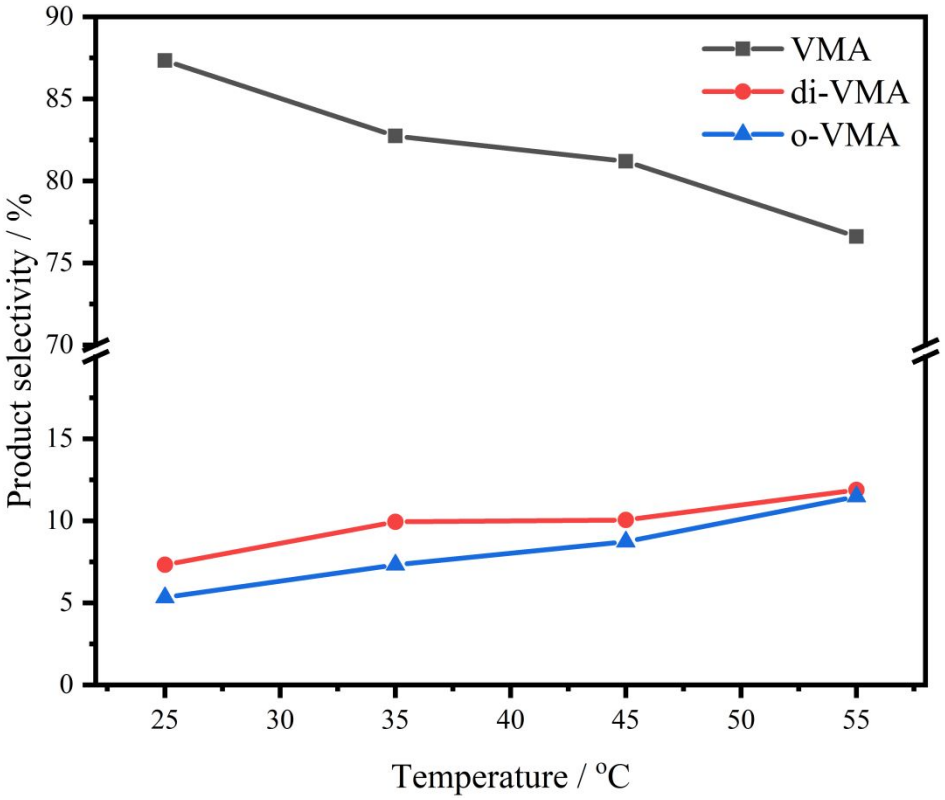

VMA
di-VMA
o-VMA
Product selectivity / %
Temperature / °C
90
85
80
75
70
15
10
5
0
25
30
35
40
45
50
55

Figure S8.

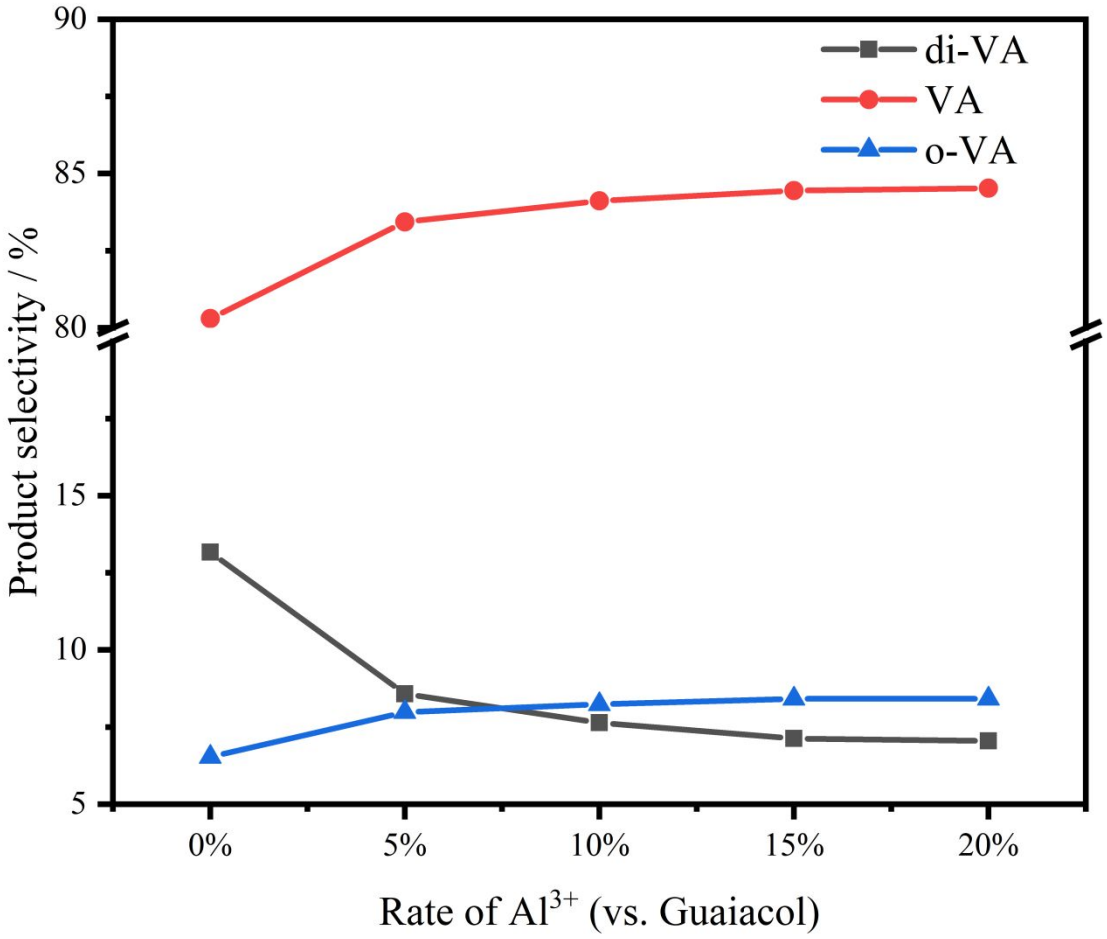

90
85
80
15
10
5
Product selectivity / %
di-VA
VA
o-VA
0%
5%
10%
15%
20%
Rate of Al3+ (vs. Guaiacol)

Figure S9.

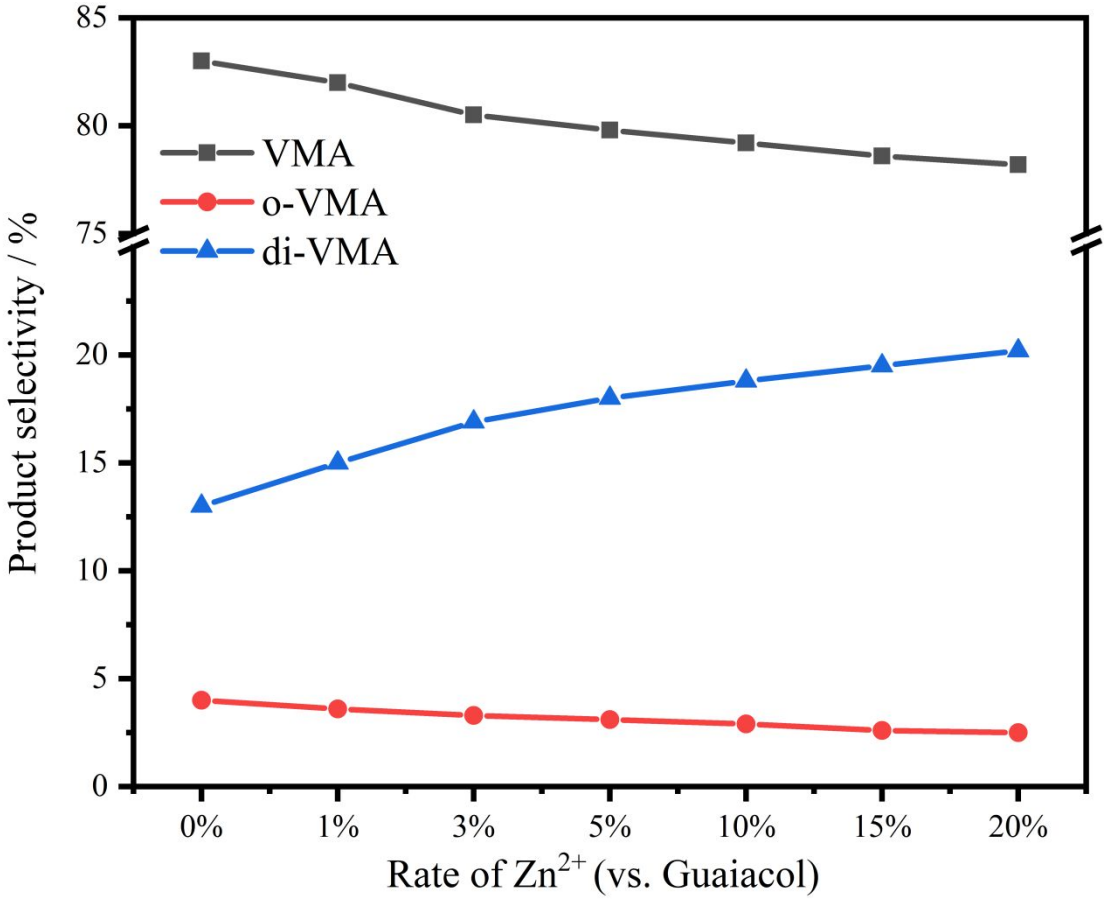

85
80
75
20
15
10
5
0
VMA
o-VMA
di-VMA
Product selectivity / %
0%
1%
3%
5%
10%
15%
20%
Rate of Zn2+ (vs. Guaiacol)

Figure S10.

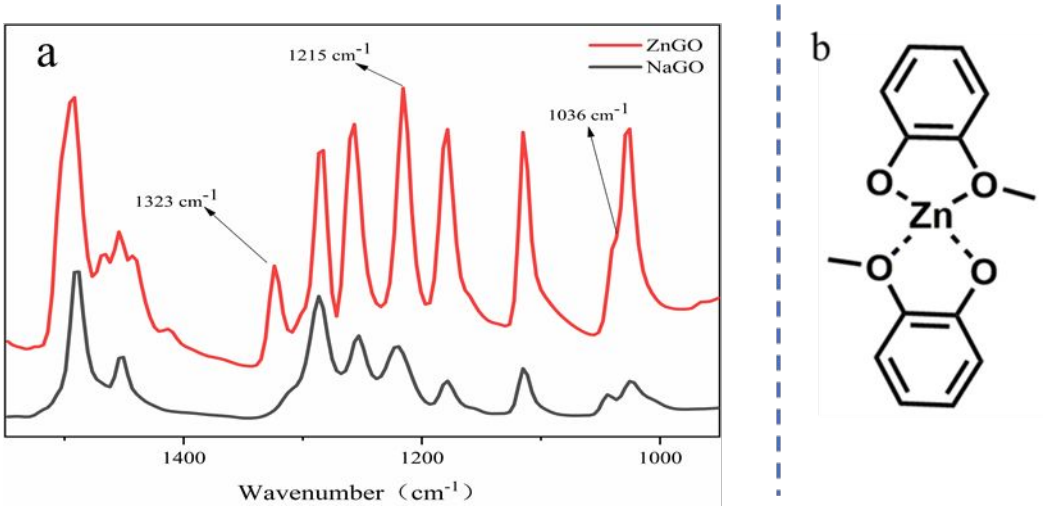
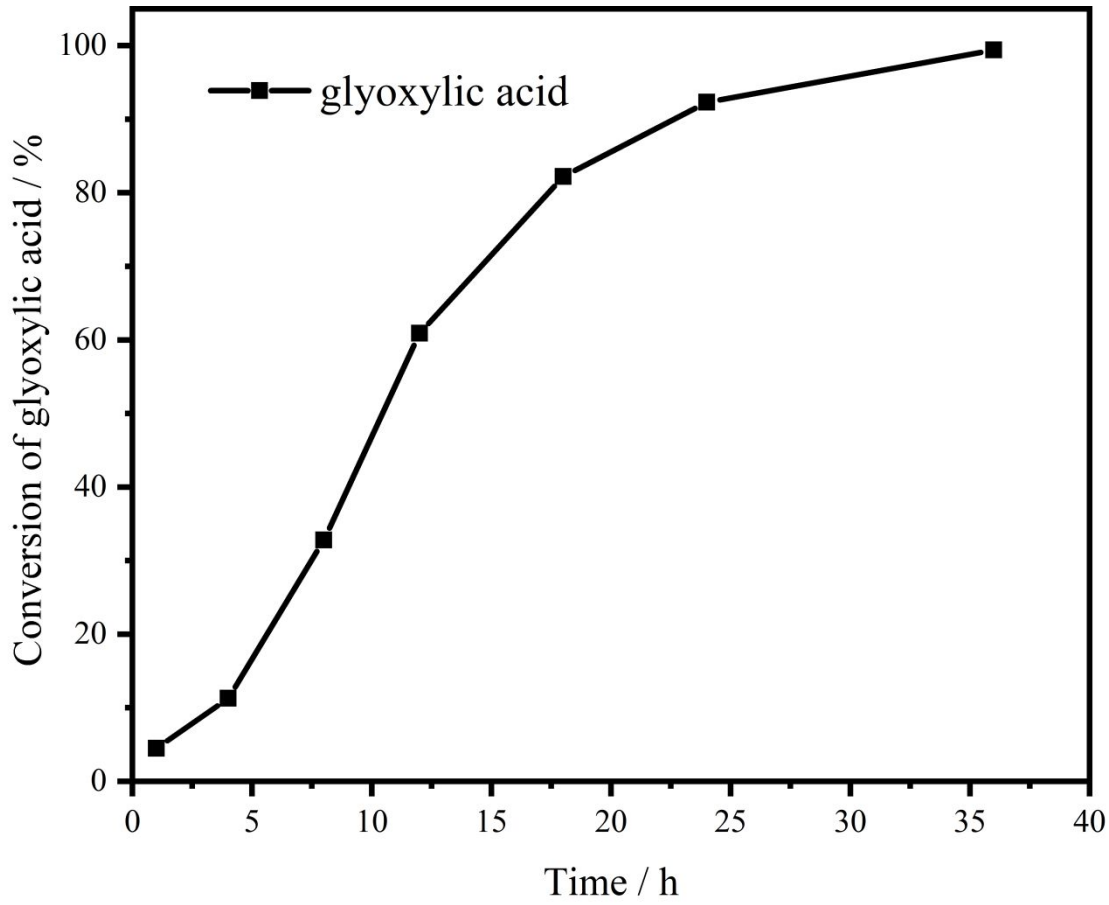

a
1215 cm-1
ZnGO
NaGO
1036 cm-1
1323 cm-1
1400
1200
1000
Wavenumber（cm-1）
b
O
O
Zn
O
O

Figure S11.


glyoxylic acid
Conversion of glyoxylic acid / %
Time / h
0
20
40
60
80
100
0
5
10
15
20
25
30
35
40