Continuous Heterogeneous Isomerization of 3/4-Methyltetrahydrophthalic Anhydride (3/4-MTHPA) with Acid and Base Modified γ- Al_2O_3 catalysts

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Electronic Supplemental Information

KOH, CH_3COOK and $KHCO_3$ salts were subjected to TG tests. SI Fig 1 shows that KOH, CH_3COOK and $KHCO_3$ have significant weight loss below 200°C, owing to the removal of crystal water in the salt. The catalyst decomposes into KOx at temperatures above 200°C, resulting in secondary weight loss. The weight tends to plateau around 600°C.

SI Fig 2 shows that weight loss occurs below 200°C, owing primarily to the removal of crystal water in the catalyst. In the test of 10%-K/Al_2O_3 and 7%-P/Al_2O_3 catalysts, there is no obvious weight loss phenomenon. Other catalysts, on the other hand, have two weight loss processes. The residual salt on the catalyst surface decomposes at temperatures above 200°C, resulting in secondary weight loss. Because of the increased loading, the calcined catalyst still contained volatiles, most likely because CH_3COOK and $NH_4H_2PO_4$ were not completely decomposed during the catalyst preparation process. The results show that the prepared catalyst's lattice is in a stable state. The addition of K and P can result in the formation of a large number of basic and acidic sites on the catalyst surface, increasing the activity of the catalyst.

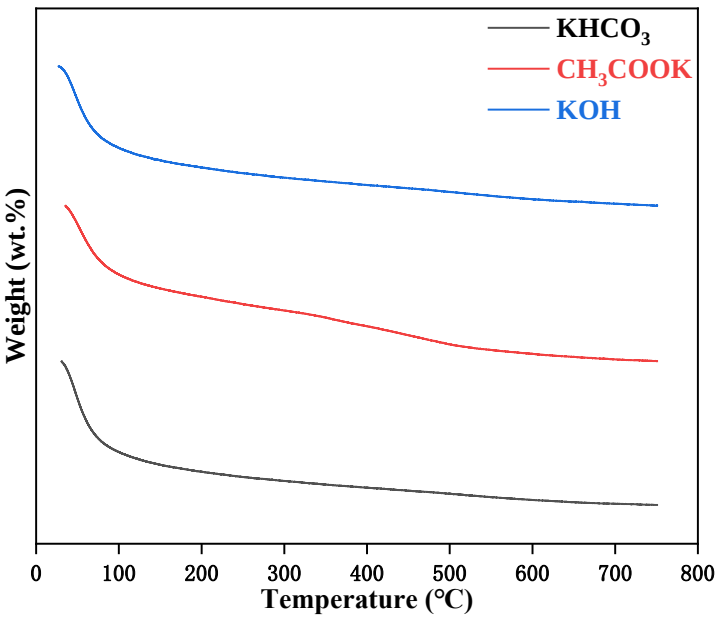

Fig 1. TG curve of the catalyst: KOH, CH_3COOK, $KHCO_3$.

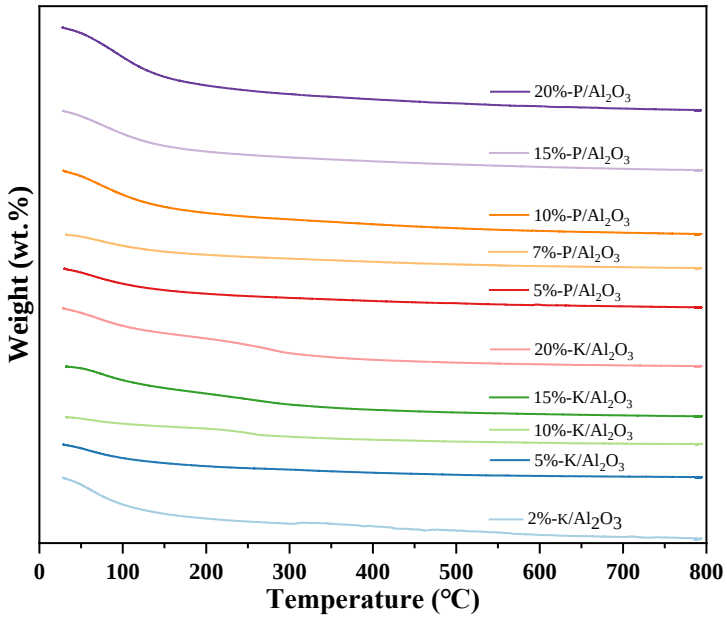

Fig 2. TG curve of the catalyst: a. X%-K/Al_2O_3 (X= 2, 5, 10, 15 and 20). b. X%-P/Al_2O_3 (X= 5, 7, 10, 15 and 20).

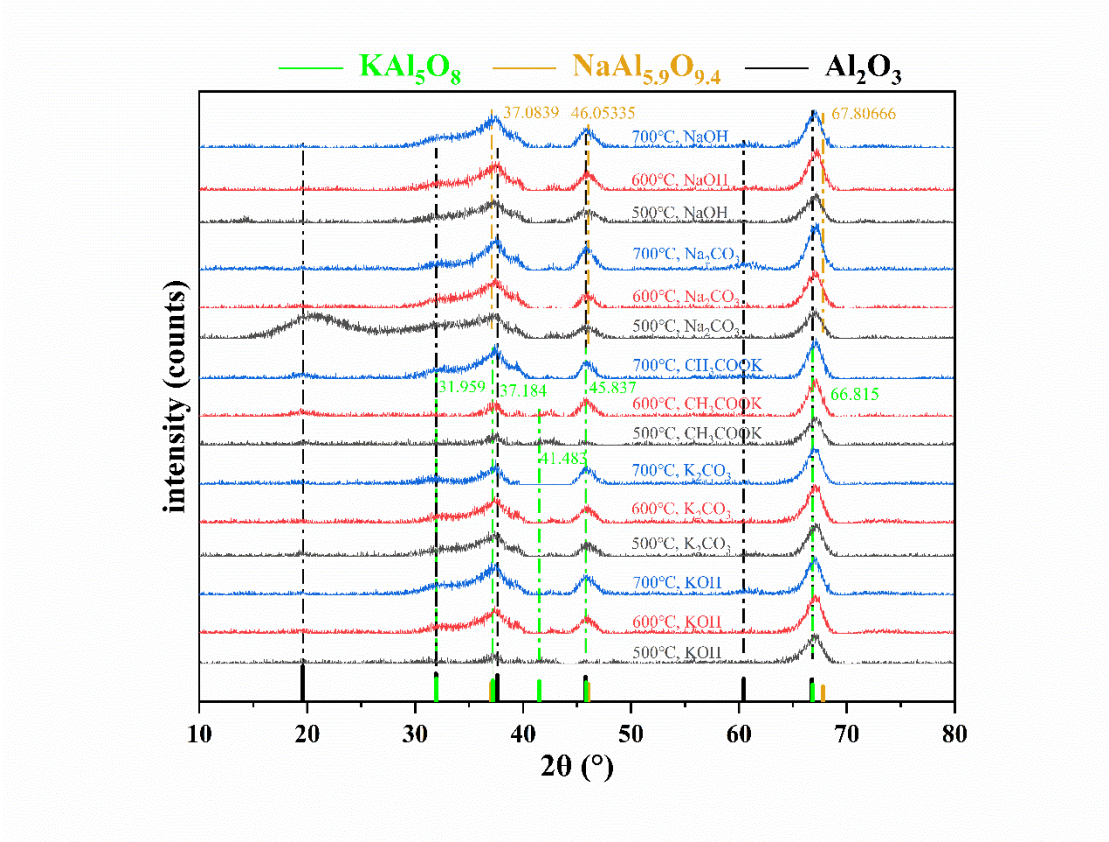

Fig 3. XRD patterns of 500 °C, 600 °C and 700 °C 2%-M/Al_2O_3 (M= CH_3COOK, K_2CO_3, KOH, NaOH and Na_2CO_3, the load of M was 2%).

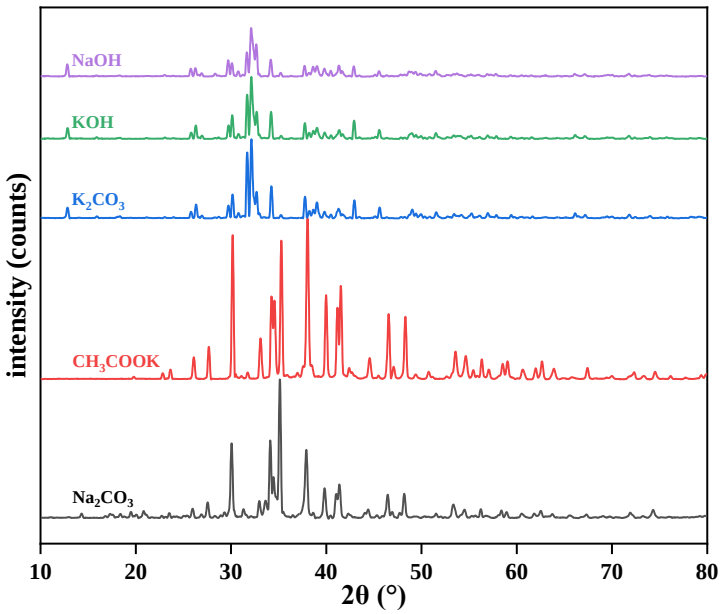

Fig 4. XRD patterns of 2%-M/Al_2O_3 (M= CH_3COOK, K_2CO_3, KOH, NaOH and Na_2CO_3, the load of M was 2%).

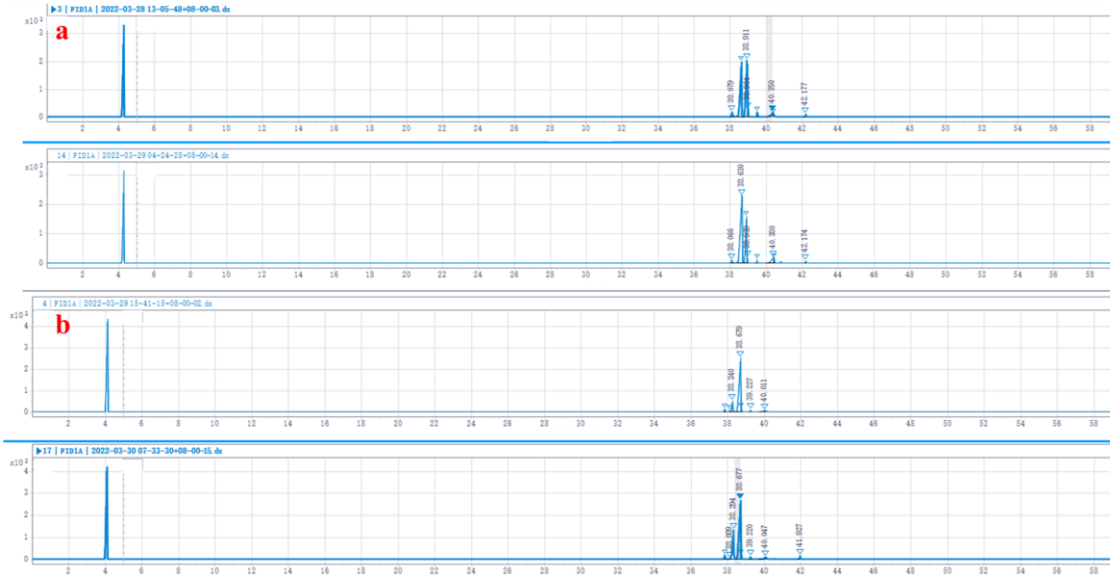

Fig. 5 Variation of component contents in the isomerization reaction of 3-MTHPA. a. Basic isomerization. b. Acid isomerization.

Based on 3/4-MTHPA, the acidic and basic isomerization of MTHPA was studied by ^{1}H-NMR. The hydrogen shift of 4-MTHPA's main functional group can be clearly seen in SI Fig 6.a. δ=5.45 is the peak segment of -C=C-H, δ=1.76 is the peak segment of -CH_3, and the coupled H peaks at other positions. SI Fig 6.b depicts the spectrum of 4-MTHPA after basic isomerization, and it is clear that the H shifts of several functional groups have changed. δ=5.5, 5.6 represents the peak segment of -C=C-H, δ=3.4~3.7 represents the peak segment of common -C-C-H, and δ=1.8~2.6 represents the peak segment of -CH_2. After basic isomerization of 4-MTHPA, the change in H-shift demonstrated the emergence of new isomers.

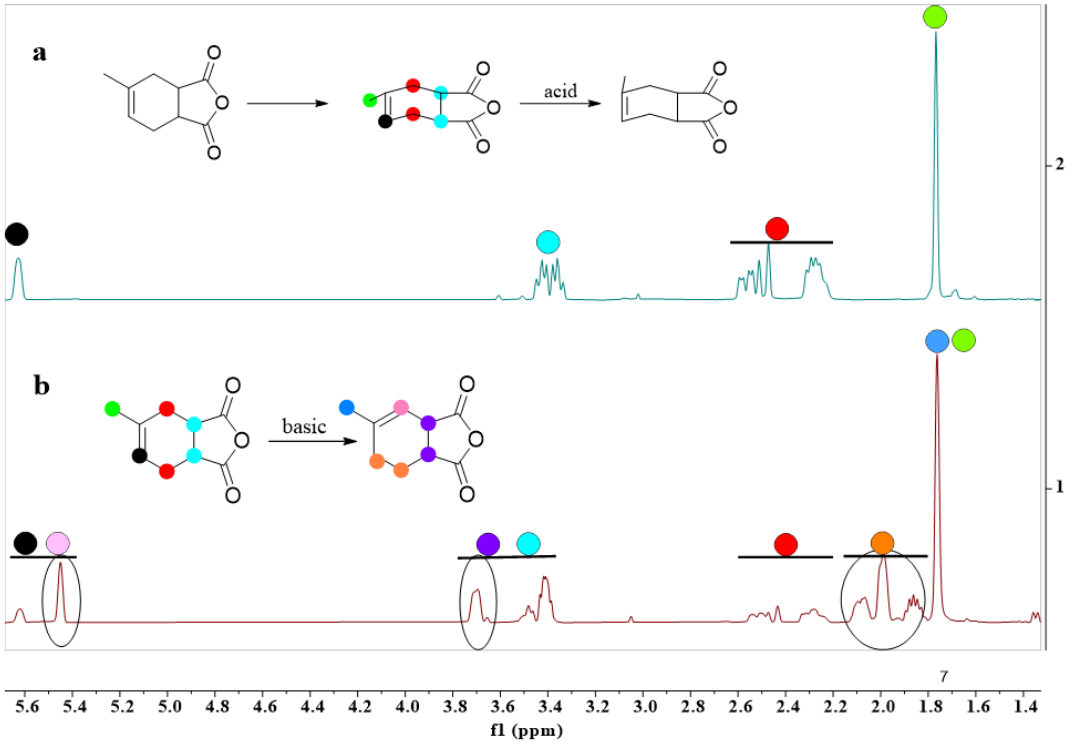

Fig 6. ^{1}H-NMR spectrum analysis. a. 4-MTHPA acid isomerization; b. 4-MTHPA basic isomerization.

SI Fig 7 depicts the ^{1}H-NMR of the acid isomerization reaction of 4-MTHPA at various temperatures, and it is discovered that the morphology of the spectrum does not change significantly. During the experiment, however, the acid isomerized product could be in a liquid state and stable at room temperature. It is possible that steric stereoisomerism modifies 4-MTHPA so that it is fluid at room temperature.

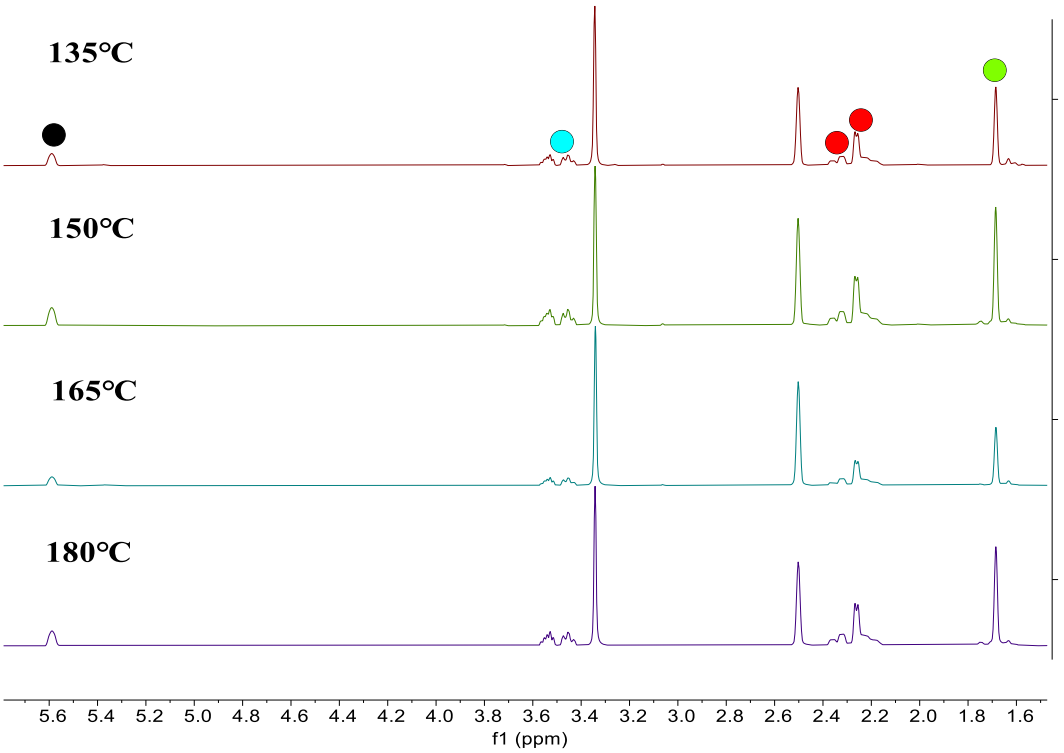

Fig 7. Basic and acid isomerization process of 4-MTHPA, and its acidic isomerization at different temperatures (T=135, 150, 165, 180℃）.

List 1. Anhydride value, viscosity, and density of 3-MTHPA basic isomerization products.

Nodes	Anhydride value (%)	Viscosity (Pa/s)	Density (g/ml 25℃)
120℃	40.96	solid	1.118
135℃	40.72	solid	1.2035
150℃	40.60	0.06290	1.2217
165℃	41.20	0.07348	1.2266
180℃	40.80	0.07744	1.2251
195℃	41.11	0.07825	1.2231
1.0h	40.60	0.06290	1.2217
1.5h	41.41	0.07292	1.2177
2.0h	41.01	0.07898	1.2164
2.5h	41.14	0.07885	1.2075
3.0h	40.87	0.07865	1.2121
3.5h	41.23	0.07891	1.2153
2%	40.87	0.07865	1.2121
5%	41.18	0.08063	1.2092
10%	40.47	0.08168	1.2116
15%	40.39	0.09421	1.2066
20%	40.68	0.11598	1.2328
0.5%	41.19	0.08040	1.2207
1.0%	40.94	0.08128	1.2223
2.0%	40.96	0.08339	1.2322
3.0%	40.39	0.09421	1.2066
4.0%	40.70	0.10628	1.2535

4-MTHPA and its isomeric products were solid at room temperature.

List 2. Anhydride value, viscosity, and density of 4-MTHPA acid isomerization products.

Nodes	Anhydride value (%)	Viscosity (Pa/s)	Density (g/ml 65℃)
120℃	40.93		1.1180
135℃	41.11		1.2035
150℃	40.55		1.2217
165℃	40.40		1.2566
180℃	39.09		1.2251
1.0h	40.40	solid	1.2217
1.5h	40.62		1.2177
2.0h	40.41		1.2164
2.5h	39.04		1.2075
3.0h	40.07		1.2121
2%	39.36		1.2121
5%	40.07		1.2092
10%	40.77	0.08553	1.2116
15%	40.07		1.2066
20%	39.89		1.2328
0.5%	39.50		1.2207
1.0%	40.19		1.2223
2.0%	40.32		1.2322
3.0%	39.36		1.2066
4.0%	40.35		1.2535

List 3. The viscosity of 3/4-MTHPA with different ratios

3/4- MTHPA ratio	Viscosity/basic (Pa/s)	Viscosity/acid (Pa/s)
3:4=1:0	solid	
3:4=1:1	0.06842	0.06040
3:4=1:1.5	0.06875	0.06090
3:4=1:2	0.07180	0.06180
3:4=2:1	0.06500	0.05810
3:4=1.5:1	0.04640	0.04290
3:4=1:0	solid	