Supporting Information

Manuscript title: *n*-Butyraldehyde Self-Condensation Catalyzed by Ce-Modified γ-Al_2O_3

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Contents

Effect of preparation conditions of γ-Al_2O_3

Alumina with different crystalline phases can be obtained from pseudo-boehmite calcinated under different conditions and its textural property will change accordingly.

1. Effect of calcination temperature

The catalytic performance of γ-Al_2O_3 prepared from pseudo-boehmite at a calcination temperature of 300 ℃, 500 ℃ and 700 ℃ for 4 h was separately investigated. It was observed that calcination temperature had little effect on the catalytic performance of γ-Al_2O_3. With the increase of calcination temperature, the conversion of *n*-butyraldehyde increased at first and then decreased but the selectivity of 2-ethyl-2-hexenal increased a little. The conversion of *n*-butyraldehyde and the yield of 2-ethyl-2-hexenal reached their highest, 83.5% and 70.8%, over the γ-Al_2O_3 calcinated at 500 ℃.

The γ-Al_2O_3 catalysts prepared at different calcination temperatures were characterized by XRD and the results are shown in Fig.S2. It can be seen that the samples obtained from pseudo-boehmite calcinated at 500 ℃ and 700 ℃ presented the crystalline phase of γ-Al_2O_3 (PDF: 48-0367). Compared with the sample obtained at 500 ℃, the diffraction peak of γ-Al_2O_3 calcinated at 700 ℃ tended to be more acute, showing that the crystallinity of γ-Al_2O_3 was higher. In contrast, the pseudo-boehmite calcinated at 300 ℃ decomposed incompletely, forming a boehmite phase (PDF: 21-1307). Combined with the catalytic performance, it was inferred that both boehmite and γ-Al_2O_3 had good catalytic performance on the self-condensation of *n*-butyraldehyde. As a consequence, for a water-generation reaction such as the self-condensation of *n*-butyraldehyde, the hydration of γ-Al_2O_3 had little influence on its catalytic performance, alleviating the deactivation caused by a poor hydrothermal stability accordingly.

2. Effect of calcination time

The catalytic performance of γ-Al_2O_3 calcinated from pseudo-boehmite at 500 ℃for different calcination times was investigated and the results are listed in Table S1. It was found that calcination time had a great effect on the catalytic performance compared with calcination temperature. With the prolonging of calcination time, the conversion of *n*-butyraldehyde and the yield of 2-ethyl-2-hexenal increased at first and then decreased while the selectivity of 2-ethyl-2-hexenal decreased gradually to a small extent. The conversion of *n*-butyraldehyde and the yield of 2-ethyl-2-hexenal reached the highest at a calcination time of 4h.

The effect of calcination time on the textural property of γ-Al_2O_3 is also shown in Table S1. It can be seen that the specific surface area reduced and the pore diameter increased but the pore volume increased at first and then decreased with the extension of calcination time. Combined with the catalytic performance, it was convinced that the bigger the pore volume, the better the catalytic performance. Under the premise of free diffusion of the reaction components in the pore, the bigger the pore volume, the more the molecule of *n*-butyraldehyde and the active sites in the pore. In this case, the self-condensation of *n*-butyraldehyde can proceed easily and the conversion of *n*-butyraldehyde increases accordingly. Therefore, the suitable preparation conditions of γ-Al_2O_3 was as follows: pseudo-boehmite was calcinated at 500 ℃ for 4 h.

Effect of reaction conditions

1. Effect of catalyst dosage

The effect of catalyst dosage on the self-condensation of *n*-butyraldehyde was investigated and the results are shown in Fig.S3. It can be seen that with the increase of catalyst dosage, the conversion of *n*-butyraldehyde increased gradually but its growth rate slowed down when the catalyst dosage was over 10 wt.%. The selectivity of 2-ethyl-2-hexenal presented a change tendency of an inverse U shape with the increase of catalyst dosage. When the catalyst dosage was up to 15 wt.%, the selectivity and yield of 2-ethyl-2-hexenal attained the highest. If the catalyst dosage is too few, the active site is not enough to catalyze the reaction and the conversion of *n*-butyraldehyde is lower. With the increase of catalyst dosage, the active sites of catalyst will increase and the catalytic activity can be improved. However, the increase of catalyst dosage can also accelerate the occurrence of side-reactions such as the Tishchenko reaction, leading to the reduction ofthe selectivity of 2-ethyl-2-hexenal.

2. Effect of reaction temperature

Fig.S4 shows the influence of reaction temperature on the self-condensation of *n*-butyraldehyde. It was observed that with the increase of reaction temperature, the conversion of *n*-butyraldehyde rose monotonically but the selectivity of 2-ethyl-2-hexenal increased at first and then reduced. The selectivity and yield of 2-ethyl-2-hexenal attained the highest at a reaction temperature of 180 ℃. The elevation of reaction temperature can be beneficial to the self-condensation of *n*-butyraldehyde but an excessive high reaction temperature will result in the Tishchenko reaction of the intermediate product 2-ethyl-3-hydroxyhexanal with *n*-butyraldehyde, reducing the selectivity of 2-ethyl-2-hexenal consequently.

3. Effect of reaction time

The effect of reaction time on the self-condensation of *n*-butyraldehyde was investigated and the results are shown in Fig. S5. What can be seen was that with the prolonging of the reaction time, the conversion of *n*-butyraldehyde increased little by little but the selectivity of 2-ethyl-2-hexenal kept around 87.0% between 4 h and 8 h. Nevertheless, when the reaction time was extended to 10 h, the selectivity of 2-ethyl-2-hexenal decreased to 83.6% due to the Tishchenko side-reaction of the target product 2-ethyl-2-hexenal with *n*-butyraldehyde to butyric acid-2-thyl-2-hexenol ester.[3] When the reaction time was 8 h, the yield of 2-ethyl-2-hexenal reached the highest.

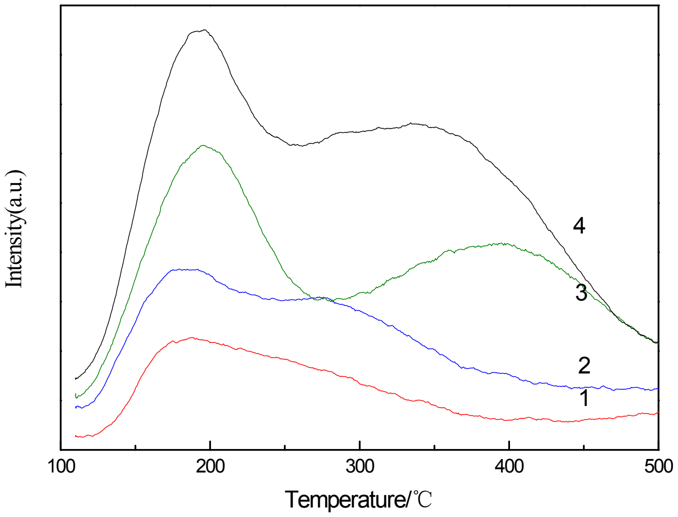


Fig. S1 NH_3-TPD profiles

1. γ-Al_2O_3，2. Hβ，3. HZSM-5(25)，4. HY

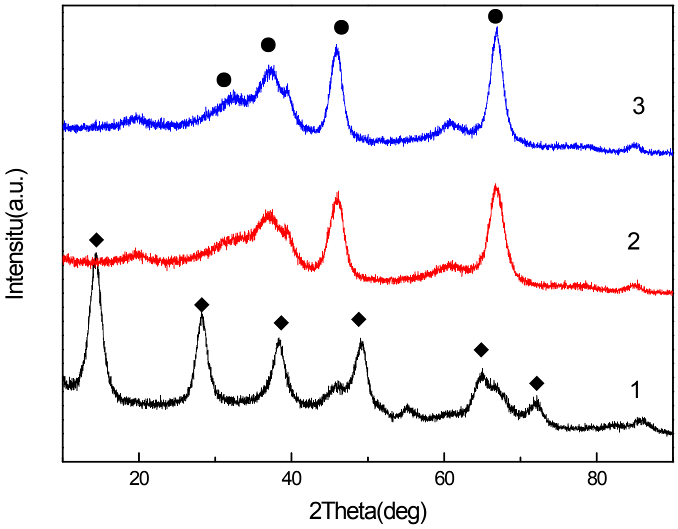


Fig.S2 XRD patterns of γ-Al_2O_3 catalysts prepared at different calcination temperatures

1.300℃，2.500℃，3.700℃

●：Al_2O_3；◆：AlO(OH)

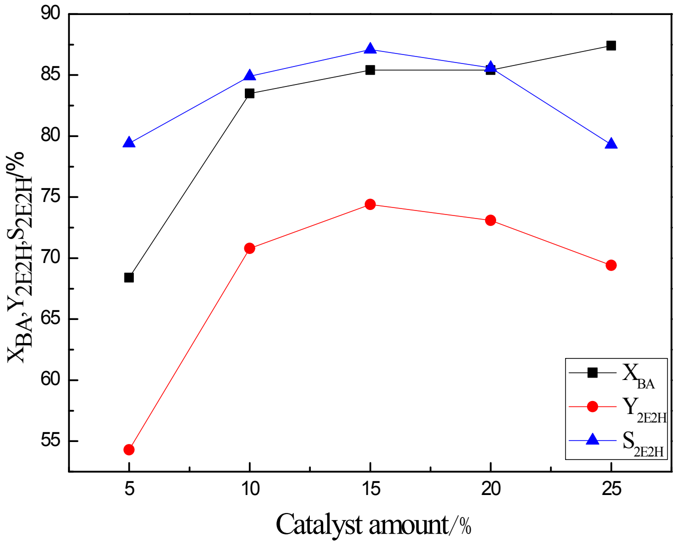


Fig.S3 Effect of catalyst amount on *n*-butyraldehyd self-condensation reaction.

Reaction conditions:T= 180 ℃, t = 6 h.

X: conversion; Y: yield; S: selectivity.BA:*n*-butyraldehyd；2E2H: 2-ethyl-2-hexenal.

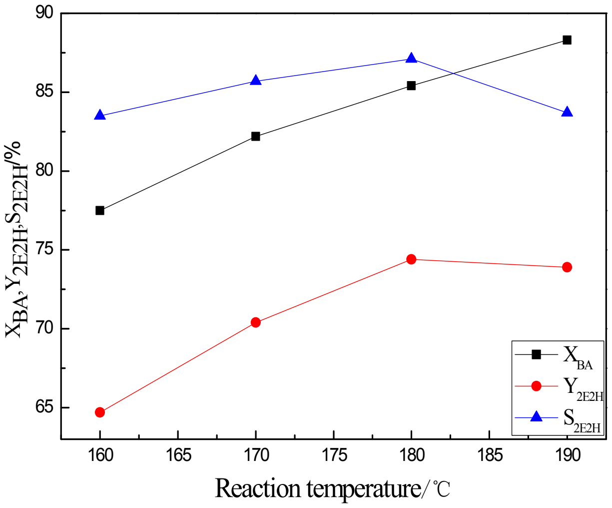


Fig.S4 Effect of reaction temperature on *n*-butyraldehyd self-condensation reaction

Reaction conditions: a weight percentage of catalyst= 15%，t = 6 h,

X: conversion; Y: yield; S: selectivity.BA: *n*-butyraldehyde；2E2H: 2-ethyl-2-hexenal.

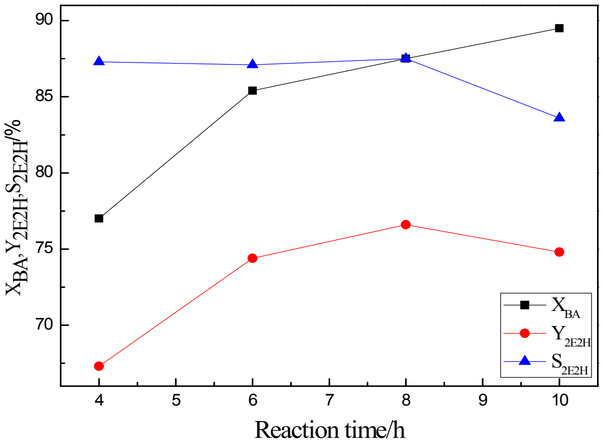


Fig.S5 Effect of reaction time on *n*-butyraldehyd self-condensation reaction
Reaction conditions: a weight percentage of catalyst=15%, T= 180 ℃.
X: conversion; Y: yield; S: selectivity; BA: *n*-butyraldehyde；2E2H: 2-ethyl-2-hexenal.

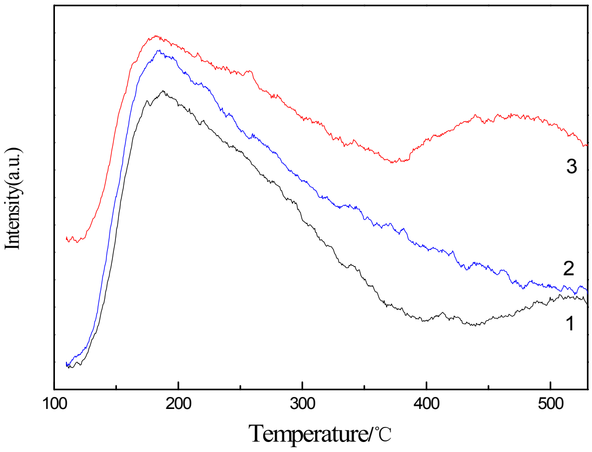


Fig.S6 NH_3-TPD profiles
1. γ-Al_2O_3， 2. B-Al_2O_3， 3. F-Al_2O_3

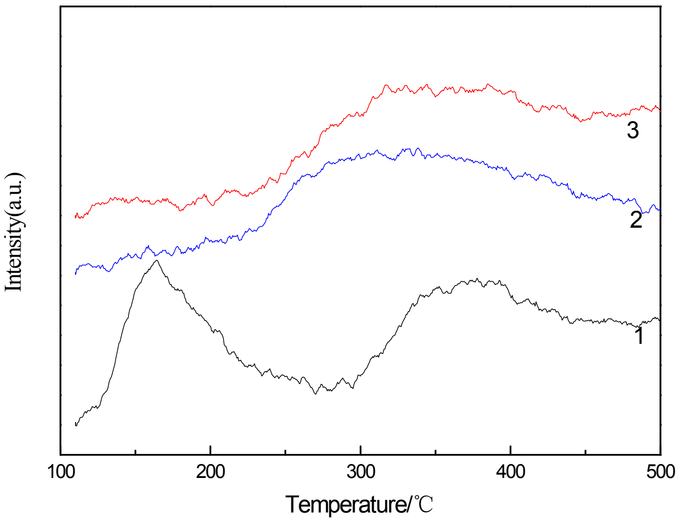


Fig.S7 CO_2-TPD profiles

1. γ-Al_2O_3， 2. B-Al_2O_3， 3. F-Al_2O_3

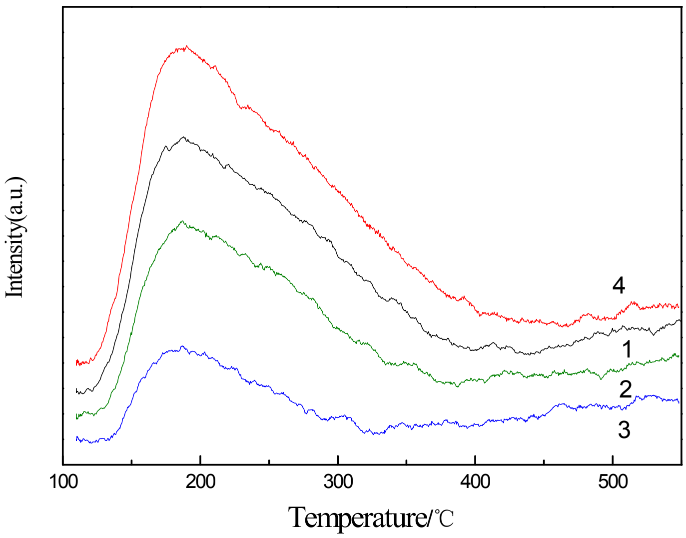


Fig.S8 NH_3-TPD profiles

1.γ-Al_2O_3， 2. Ba-Al_2O_3， 3. K-Al_2O_3， 4. Mg-Al_2O_3

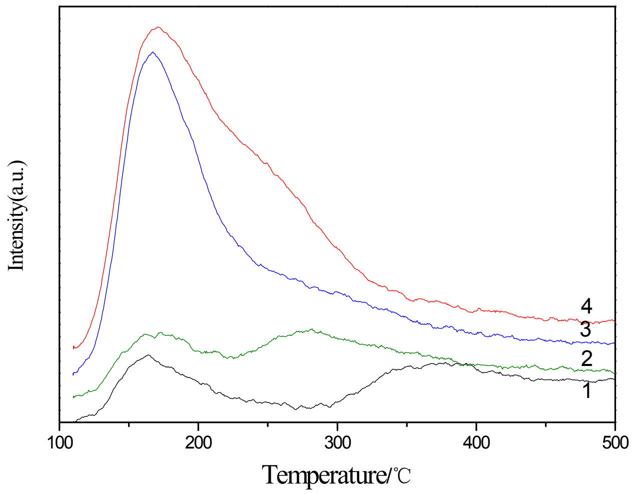


Fig.S9 CO_2-TPD profiles

1.γ-Al_2O_3，2. Ba-Al_2O_3，3. K-Al_2O_3，4. Mg-Al_2O_3

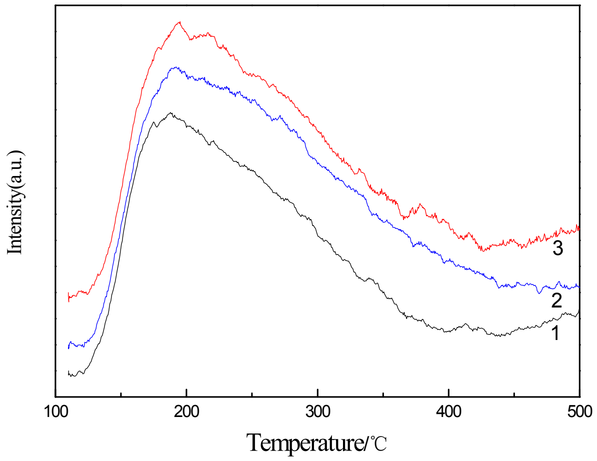


Fig.S10 NH_3-TPD profiles

1. γ-Al_2O_3，2. Zn-Al_2O_3，3. Ce-Al_2O_3

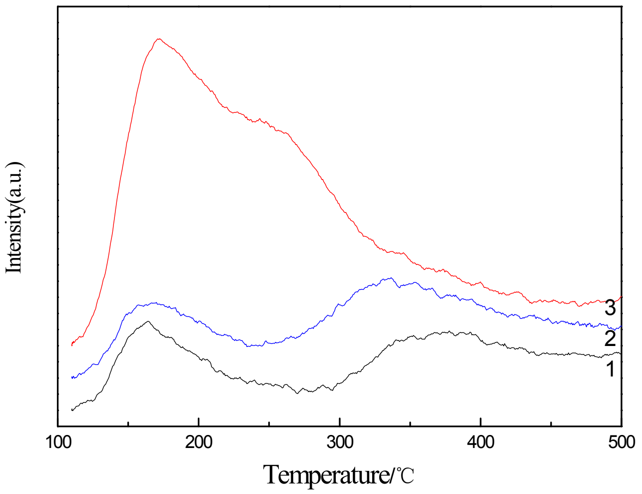


Fig.S11 CO$_2$-TPD profiles

1. γ-Al$_2$O$_3$，2. Zn-Al$_2$O$_3$，3. Ce-Al$_2$O$_3$

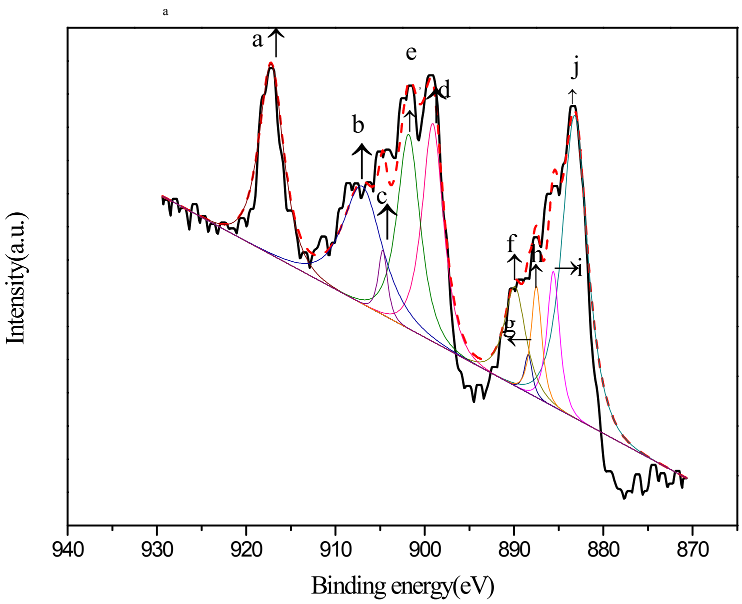


Fig.S12 XPS spectra of Ce 3d of the fresh Ce-Al$_2$O$_3$

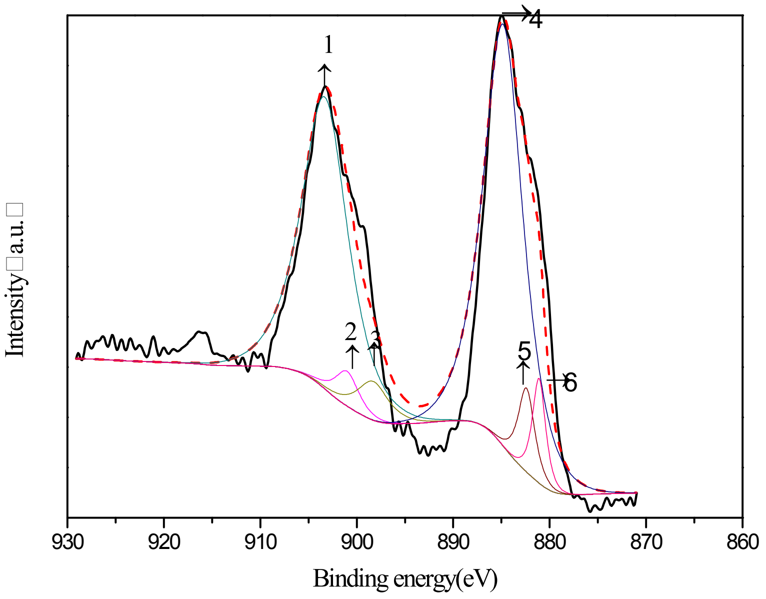


Fig.S13 XPS spectra of Ce 3d of the recovered Ce-Al_2O_3without calcination

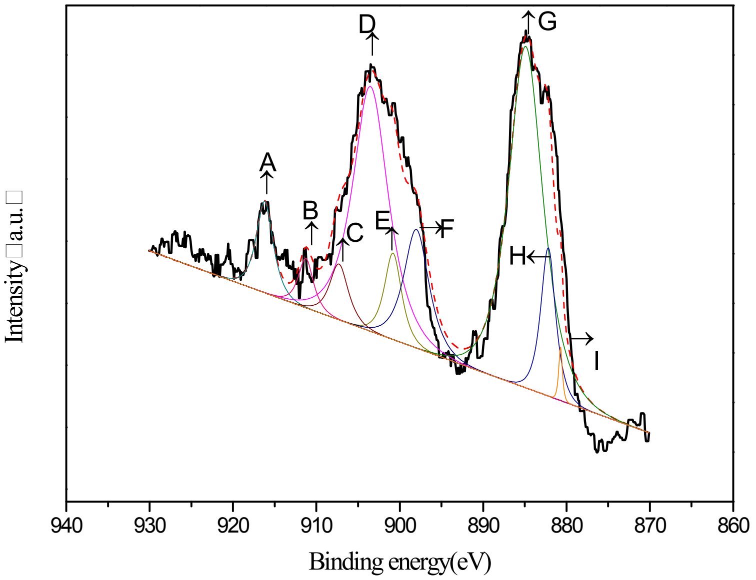


Fig.S14 XPS spectra of Ce 3d of the recovered Ce-Al_2O_3 after calcination

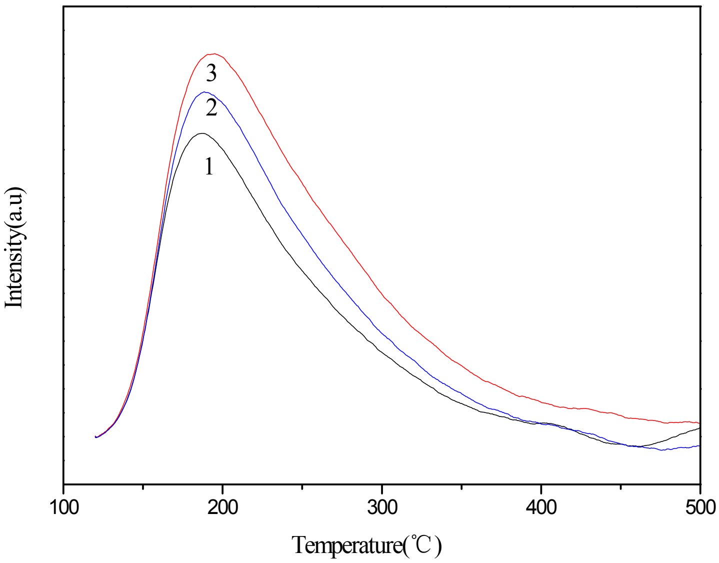


Fig.S15 CO_2-TPD profiles

1. Fresh Ce-Al_2O_3, 2.Recovered Ce-Al_2O_3 after calcination,

3. Recovered Ce-Al_2O_3 without calcination

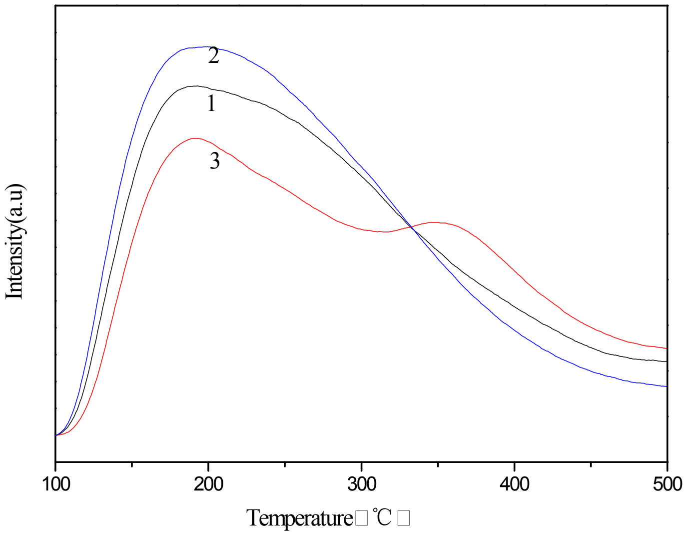


Fig.S16 NH_3-TPD profiles

1. Fresh Ce-Al_2O_3, 2.Recovered Ce-Al_2O_3 after calcination,

3. Recovered Ce-Al_2O_3 without calcination

Table S1 Effect of calcination time on the catalytic performance and textural property of γ-Al_2O_3

Calcination time /h	Specific surface area /m^2.g^{-1}	Pore volume /cm^3.g^{-1}	Pore diameter /nm	X_{BA} /%	Y_{2E2H} /%	S_{2E2H} /%
2	243	0.356	4.51	80.7	68.8	85.2
4	230	0.359	4.71	83.5	70.8	84.9
6	226	0.336	4.91	78.6	66.4	84.5

Reaction conditions: a weight percentage of catalyst=10%, T=180℃, t = 6h.

Table S2 Acid and base properties of the fresh and recovered Ce-Al_2O_3 catalysts

	Base property		Acid property				
			NH_3 desorption peak at lower temperature		NH_3 desorption peak at higher temperature		Total acid amount /μmol·g^{-1}
Catalyst	CO_2 desorption peak /℃	Total base amount/ μmol·g^{-1}	Peak top temperature /℃	Weak acid amount /μmol·g^{-1}	Peak top temperature /℃	Strong acid amount /μmol·g^{-1}	
Fresh Ce-Al_2O_3	187.3	540.3	191.9	404.8	-	-	404.8
Recovered without calcination	195.1	651.0	187.4	223.4	351.0	117.7	340.1
Recovered after calcination	188.2	582.9	192.4	425.6	-	-	425.6

Table S3 Identification of the components in the reaction system of *n*-butyraldehyde aldol condensation over Ce-Al_2O_3

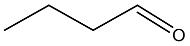
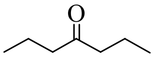
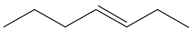
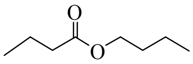
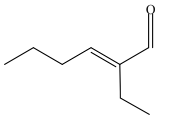
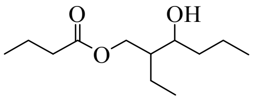
Retention time/min	Components	Structure	Similarity	Peak area	Relative content/%
2.14	*n*-butyraldehyde		100	967793	6.23
4.68	4-heptanone		81.29	218025	1.40
5.73	3-heptene		91.37	105213	0.68
7.07	butyl butyrate		79.89	167637	1.08
9.78	2-ethyl-2-hexenal		100	13987464	90.03
13.63	2-ethyl-3-hydroxyhexyl butyrate		94.76	89511	0.58

Table S4 Conversion of *n*-butyraldehyde at different reaction temperatures and reaction times

t/s	x_A/%				
	120℃	130℃	140℃	160℃	180℃
0	7.85	11.30	16.12	29.03	36.20
3600	32.64	47.21	48.49	65.77	62.99
7200	48.01	51.37	61.68	73.03	75.89
10800	55.72	61.21	70.12	81.01	84.84
14400	59.01	65.22	74.25	83.89	89.24
21600	66.12	71.22	76.36	88.83	91.97
28800	70.68	75.46	83.31	91.11	93.17