# Supporting Information

## Regulation of hydrogenation products of fatty acid by tuning the acidity of

## cobalt catalyst

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## Experimental

### Materials

$Co(NO_3)_2 \cdot 6H_2O$ (99.0%), NaOH (≥98%), and $NH_3 \cdot H_2O$ (28% in $H_2O$,≥99.9%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. n-octanoic acid (99.0%), n-octanol (99.5%), n-octanal (99.0%), octyl octanoate (98.0%), n-octane (99.0%), n-heptane (99.0%), $Na_2CO_3$ (≥99.9%), $(NH_4)_2CO_3$ (99.0%) and dichloromethane (99.5%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All the reagents were used without further purification. Nitrogen (99.9%) and hydrogen (99.9%) were purchased from Zhuhai Huaxin Gas Co., Ltd.

### Catalyst preparation

$Co_3O_4$, as precursors of Co catalysts, were prepared by the precipitation method using different precipitants. In the typical process, 60 mmol of cobalt nitrate was dissolved in 200 mL distilled water, and 0.345 M of aqueous precipitants (NaOH, $Na_2CO_3$, $(NH_4)_2CO_3$, $NH_3 \cdot H_2O$, respectively) was added dropwise into the cobalt nitrate solution using peristaltic pump under vigorous stirring until the mixture reached pH 9. Then, the suspension was kept stirring at 65 °C for 1 h before aged at room temperature for 12 h. The obtained precipitate was separated by filtration and thoroughly washed with distilled water for several times to achieve a near-neutral pH washing liquor. The solid product was dried at 100 °C for 12 h and then calcined in a furnace under static air atmosphere at 450 °C for 4 h to obtain $Co_3O_4$. Accordingly, the prepared catalysts were labeled as $Co_3O_4$-NaOH, $Co_3O_4$-$Na_2CO_3$, $Co_3O_4$-$(NH_4)_2CO_3$ and $Co_3O_4$-$NH_3 \cdot H_2O$ based on the precipitant used.

The $Co_3O_4$ precursor was further reduced at 400 °C for 2 h under flowing $H_2$ (10% $H_2$-90%$N_2$ mixed gas) in tube furnace with a ramp of 5 °C/min before reaction, and the obtained catalysts were denoted as Co-NaOH, Co-$Na_2CO_3$, Co-$(NH_4)_2CO_3$ and Co-

NH₃·H₂O, respectively.

## Catalyst characterization

Field emission scanning electron microscopic (FE-SEM) images of samples were obtained using a Thermo Fisher Apreo 2C emission scanning electron microscope. The X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV apparatus using Ni-filtered Cu Kα radiation (λ=0.154nm) at 40 mA and 40 kV. The samples were scanned from 10 to 80º with a step size of 0.02º and counting time of 2 s per step.

The $NH_3$-TPD was carried out on BELCAT II+BELMASS II equipped with a TCD. Prior to each experiment, the catalyst (50 mg) was pre-treated in flowing pure He (30 mL/min) at 150 ºC for 30 min and then cooled to 40 ºC and maintained 5 min. Then, the gas was switched to 10%$NH_3$/90%He and holding at 40 ºC for 60 min before switched back to He (30 mL/min) for 60 min until the baseline was stable and the physically adsorbed $NH_3$ were fully desorbed. Finally, the temperature was increased at a rate of 10 ºC/min to 800 ºC in flowing He (30 mL/min) until the end of the experiment. $H_2$-TPD experiments were performed in the same apparatus as $NH_3$-TPD. A 50-mg sample was heated from room temperature to 200 ºC at a rate of 10 ºC/min and swept with 50 mL/min He flow for 30 min. Then, the sample was cooled to 30 ºC, and switch to 50 mL/min 5%$H_2$/95%Ar and holding for 60 min. After removing the physically adsorbed $H_2$ by flush with He, the samples were heated to 800 ºC in He at a rate of 10 ºC/min.

## Catalytic activity tests

The catalytic experiments in this paper were performed in a mini batch reactor with an internal volume of 5 mL, containing an air inlet and an air outlet. The reactor can withstand the maximum pressure of 25 MPa and the maximum temperature of 400 ºC. The upper part of the reactor is connected with a pressure gauge to facilitate the

detection of pressure during the reaction. Before the reaction, 0.2 ml n-Octanoic acid, 20 mg catalyst, and 3 mL n-hexane as solvent were added into the reactor. The magnetons (Teflon magnetic stirrer, which provides agitation during the reaction) were also added into each mini reactor and the rotation speed was set at 500 rpm. After sealing the reactors, $N_2$ was purged into reactor to remove the air and this process was repeated 3 times. Afterwards, $H_2$ was purged into the reactor to remove $N_2$ through the air intake and this process was repeated for 3 times, and at last $H_2$ was purged to reach 2 MPa pressure, i.e., a pre-pressure before heating. The sealed high-pressure reactors were heated to a pre-set temperature in the reactor heating jacket, and after reaching the required reaction time, they were automatically cooled to room temperature. After that, the products in the reactor and the unconverted reactants were extracted and diluted by adding 10 mL of dichloromethane, and then analyzed qualitatively and quantitatively.

**Analysis method**

The liquid reaction products were identified by matching the retention times of the gas chromatograph to those of the reference standards, and were quantified by a gas chromatograph (Agilent 6850) equipped with an Agilent CP-FFAP column and flame ionization detector (FID). Nitrogen was used as a carrier gas at a volume flow rate of 5 mL/min. The temperatures of the injector and detector were set to 300 ℃ and 250 ℃, respectively. Calibration curves for each compound were used for quantitative analysis. At the rate of 10 ℃/min, programmed temperature rises to the set temperature (250 ℃). The split ratio of the liquid is 10. The conversion of reactants was calculated as the moles of reactants consumed divided by the initial moles of reactants added to the reactor. The yield of each product was calculated as the moles of the recovered product divided by the moles of the reactant feeding. The reactant conversion and product yield are calculated using the following formula. The reported uncertainty is the standard

deviation determined from three repeated experiments. All experiments were repeated at least twice with an error of less than 5%, and the data shown in this work are the average of the repeated experiments. Based on GC results, the conversion, selectivity, and yield of products were calculated by the following formula:

$$Conversion(\%) = 1 - \frac{mole\ of\ remained\ reactant(C_t)}{mole\ of\ feeded\ reactant(C_o)} \times 100\%$$

$$Yield(\%) = \frac{mole\ of\ product(C_p)}{mole\ of\ feeded\ reactant(C_o)} \times 100\%$$

$$Selectivity(\%) = \frac{Yield(\%)}{Conversion(\%)} \times 100\%$$