

# Un-modified Bulk Alumina as an Efficient Catalyst for Propane Dehydrogenation

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## 1. Materials

$\gamma$ -Al<sub>2</sub>O<sub>3</sub>-100,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-200 and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>-90 were provided by Sasol company. They are used directly without any modification in this study.

## 2. Characterization

X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-2550 PC diffractometer from 5° to 50° with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , 40kV, 40mA) and scan speed of  $2\theta = 8.0^\circ/\text{min}$ .

Nitrogen adsorption measurement was performed on a Micromeritics@ASAP2420 at 77 K. Samples were treated in vacuum for 2 h at 300 °C before the measurement. The BET method and BJH model were applied for the calculation of the pore size distribution and surface area, respectively.

The temperature-programmed desorption of ammonia technique was recorded on a conventional flow system equipped with a thermal conductivity detector. Prior to the NH<sub>3</sub>-TPD test, the catalyst was calcined at 900 °C and then cooled to room temperature. The sample was treated with 5% NH<sub>3</sub> at the room temperature. The NH<sub>3</sub>-TPD experiment was performed under a flow of N<sub>2</sub> from 200 to 900 °C with a rate of 10°C/min.

Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with an (*in-situ*) cell was used for the pyridine adsorption on Al<sub>2</sub>O<sub>3</sub>. A self-supporting pellet about 10 mg was mounted into the cell and heated at 973 K for 4 h under a vacuum, followed by cooling

to room temperature. The pyridine vapor was introduced into the cell, and then evacuated at 473 and 573 K for 30 min. Spectra were taken at evacuation temperature in the 1700-1400  $\text{cm}^{-1}$  by using coaddition with 32 scans. The amount of the Lewis acid sites in samples was calculated from the following method:  $C(\text{pyridine on L sites})=1.42IA(L)R^2/W$ .  $C$ =concentration (mmol/g catalyst);  $IA$ =integrated absorbance of L band at 1450  $\text{cm}^{-1}$ ;  $R$ =radius of catalyst disk (cm);  $W$ =weight of disk (mg).

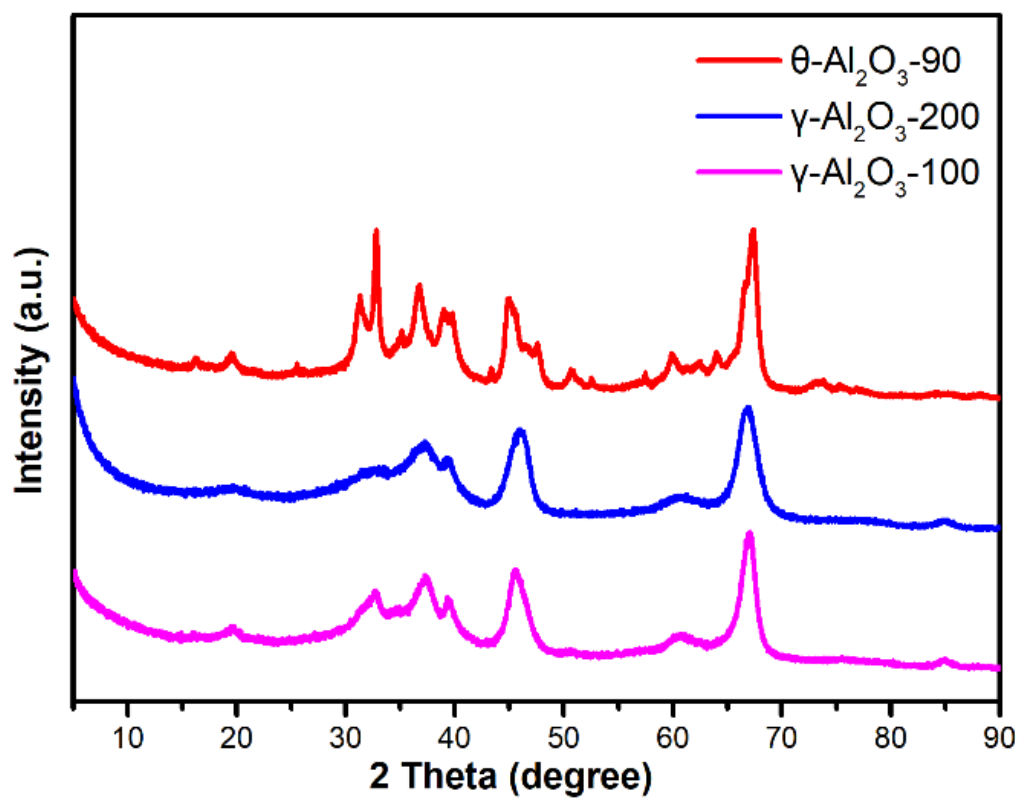
The *in-situ* IR of  $\text{C}_3\text{H}_8$  adsorption on  $\text{Al}_2\text{O}_3$  was carried out in a Nicolet iS50. The  $\text{Al}_2\text{O}_3$  pellet was kept into an IR cell, followed by a thermal treatment at 700 °C in the flow of  $\text{N}_2$  to eliminate any physically adsorbed  $\text{H}_2\text{O}$ . Propane gas was introduced into the cell, after the cell was cooled to room temperature. Prior to the measurement, the sample was degassed with a vacuum pump at 50, 100 and 100 °C for 2 h.

### 3. Catalytic reaction

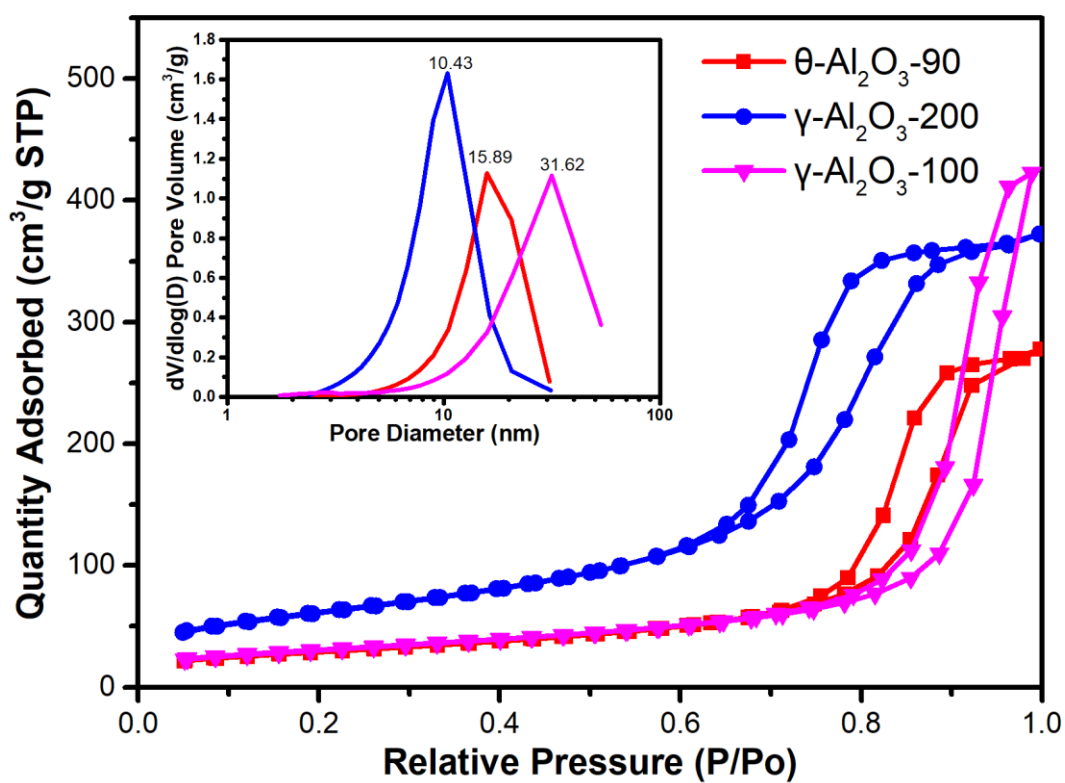
Propane dehydrogenation reaction was carried out in a quartz tube fixed-bed reactor at 630 °C under the atmospheric pressure. 2 g of  $\text{Al}_2\text{O}_3$  sample was pressed into the pellet with a size from 200 to 400  $\mu\text{m}$ . The catalyst was loaded into the reactor with a diameter of 10 mm. The sample was activated at 700 °C before the catalytic test. A feed mixture of 10 mol %  $\text{C}_3\text{H}_8$ /10 mol %  $\text{H}_2$ /80 mol %  $\text{N}_2$  was introduced into the reactor with a flow rate of 45 ml/minute, which corresponds to the weight hourly space velocity of 0.26  $\text{h}^{-1}$ . The products were analyzed with an online GC equipped with the flame ionization detector (FID) and thermal conductivity detector (TCD).

The carbon balance of propane dehydrogenation over these  $\text{Al}_2\text{O}_3$  samples was evaluated by comparing the number of moles of carbon in the outlet stream to the number of moles of carbon in the feed. Under the typical evaluating conditions, the

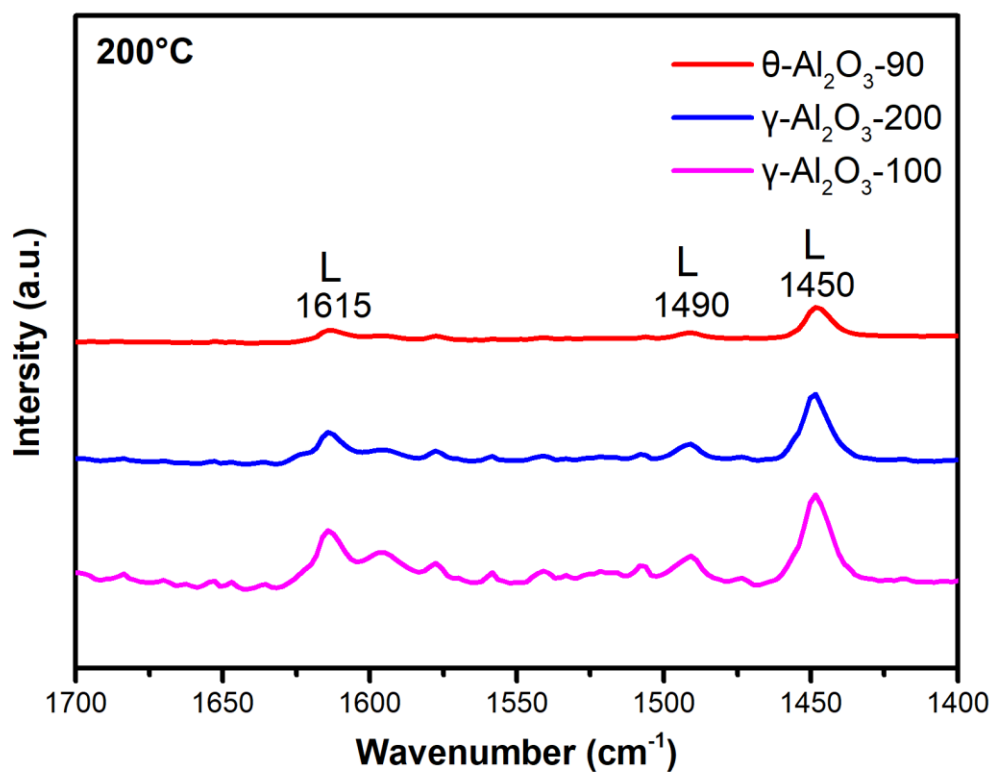
carbon balance was above 97%. The propane conversion and propylene selectivity were calculated from following equation: propane conversion (%) =  $([F_{C_3H_8}]_{in} - [F_{C_3H_8}]_{out}) / [F_{C_3H_8}]_{in}$ ; propylene selectivity (%) =  $[F_{C_3H_6}]_{out} / ([F_{C_3H_8}]_{in} - [F_{C_3H_8}]_{out})$ .



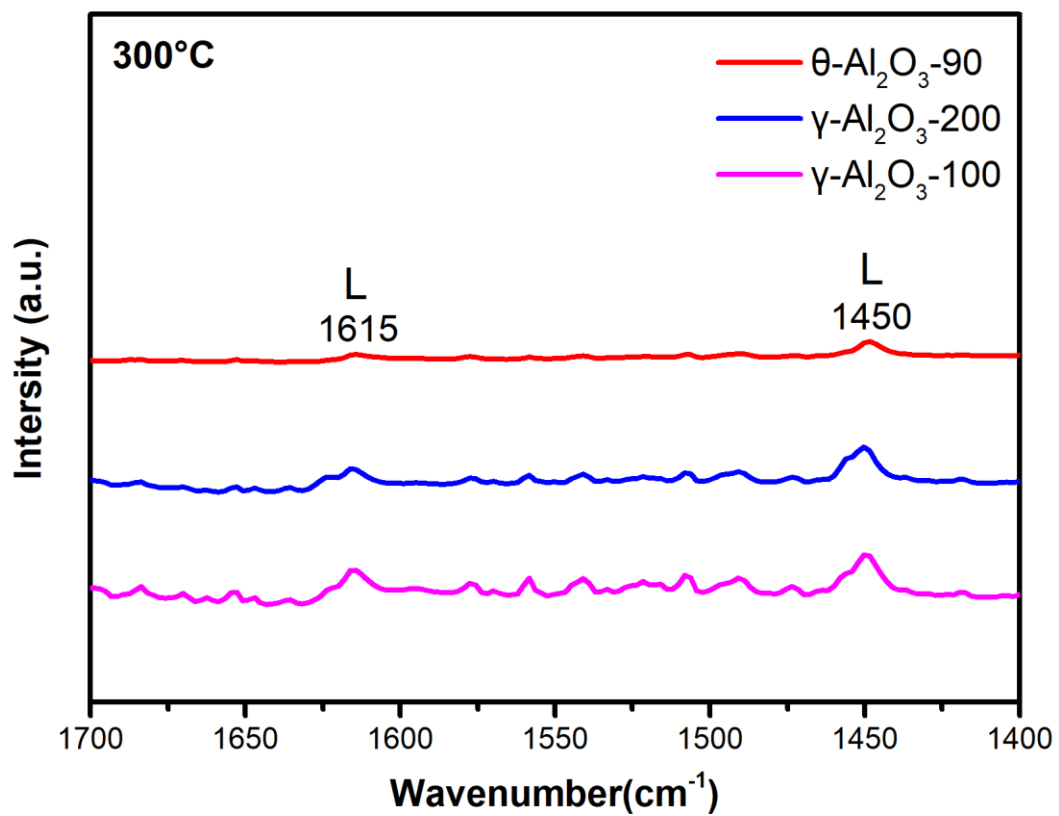
**Figure S1.** XRD patterns of different  $\text{Al}_2\text{O}_3$  catalysts.



**Figure S2.** Nitrogen adsorption and corresponding pore size distribution of different  $\text{Al}_2\text{O}_3$  catalysts.

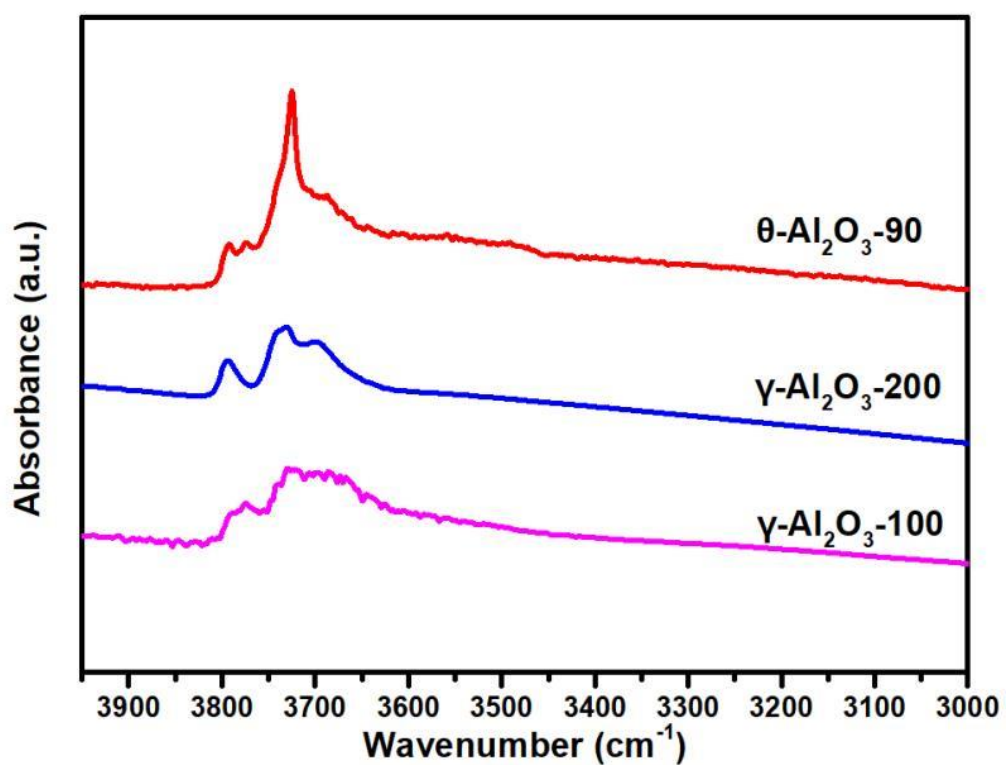


**Figure S3.** FTIR spectra of pyridine adsorbed on different Al<sub>2</sub>O<sub>3</sub> catalysts at 200 °C.

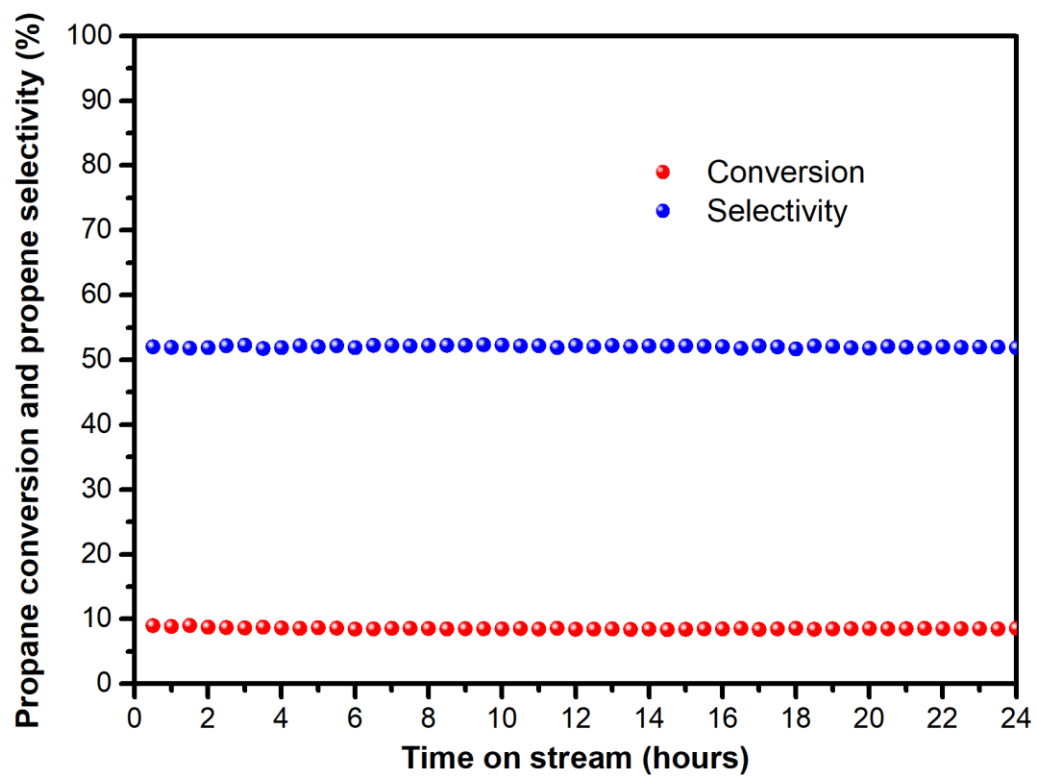


**Figure S4.** FTIR spectra of pyridine adsorbed on different Al<sub>2</sub>O<sub>3</sub> catalysts at 300 °C.

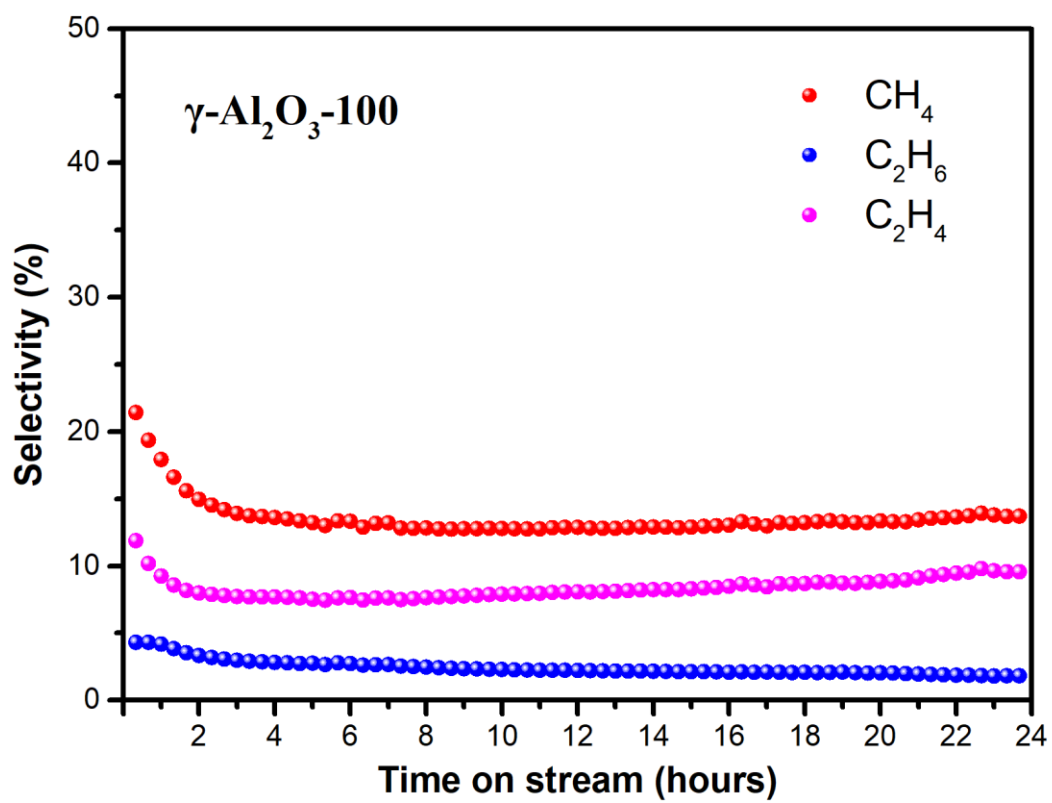




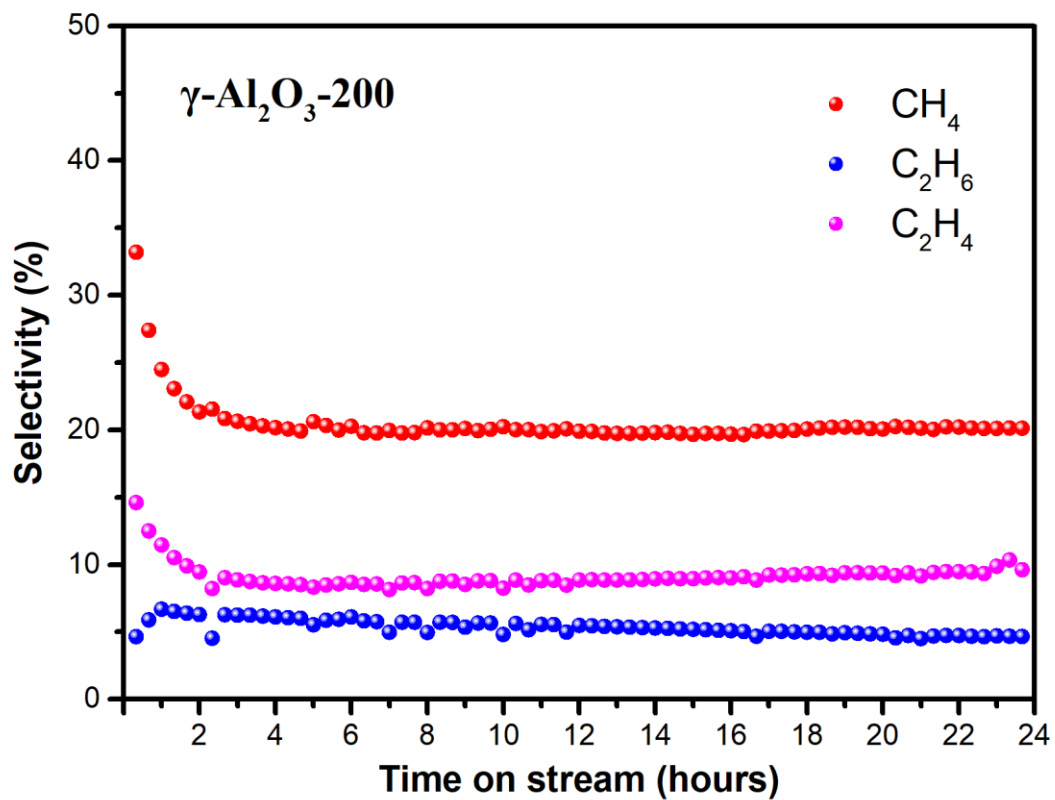
**Figure S5.** FTIR spectra of different Al<sub>2</sub>O<sub>3</sub> in the spectra region of 3950-3000 cm<sup>-1</sup>.



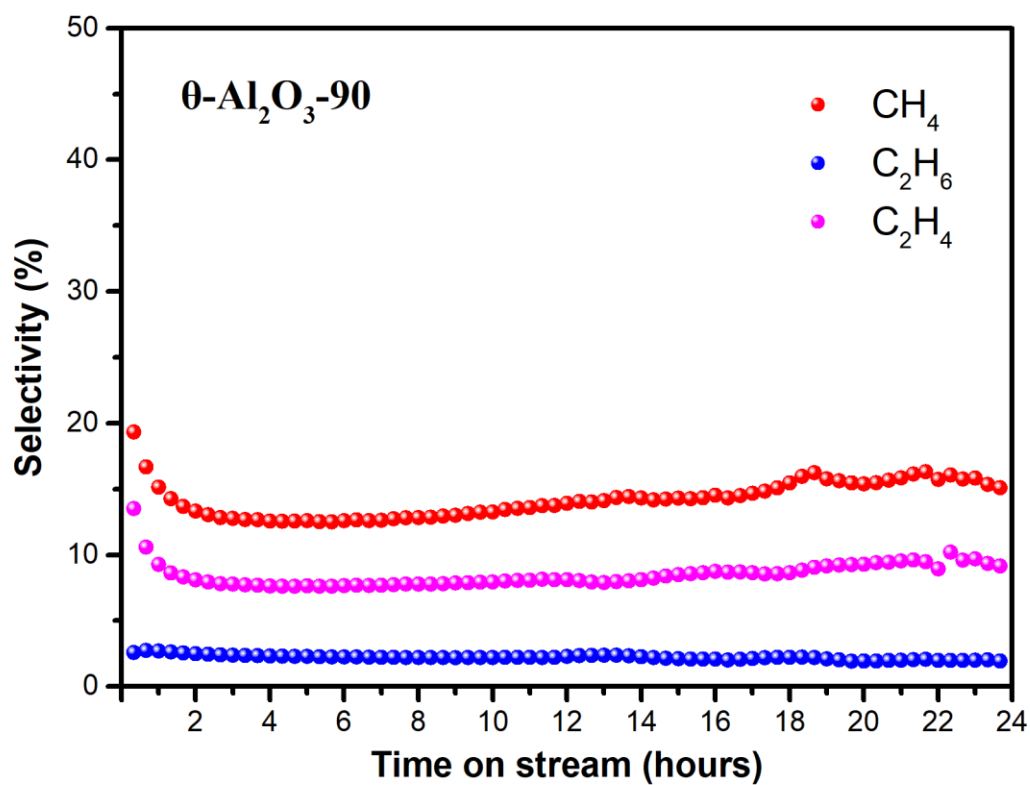
**Figure S6.** Catalytic performance of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in propane dehydrogenation reaction.



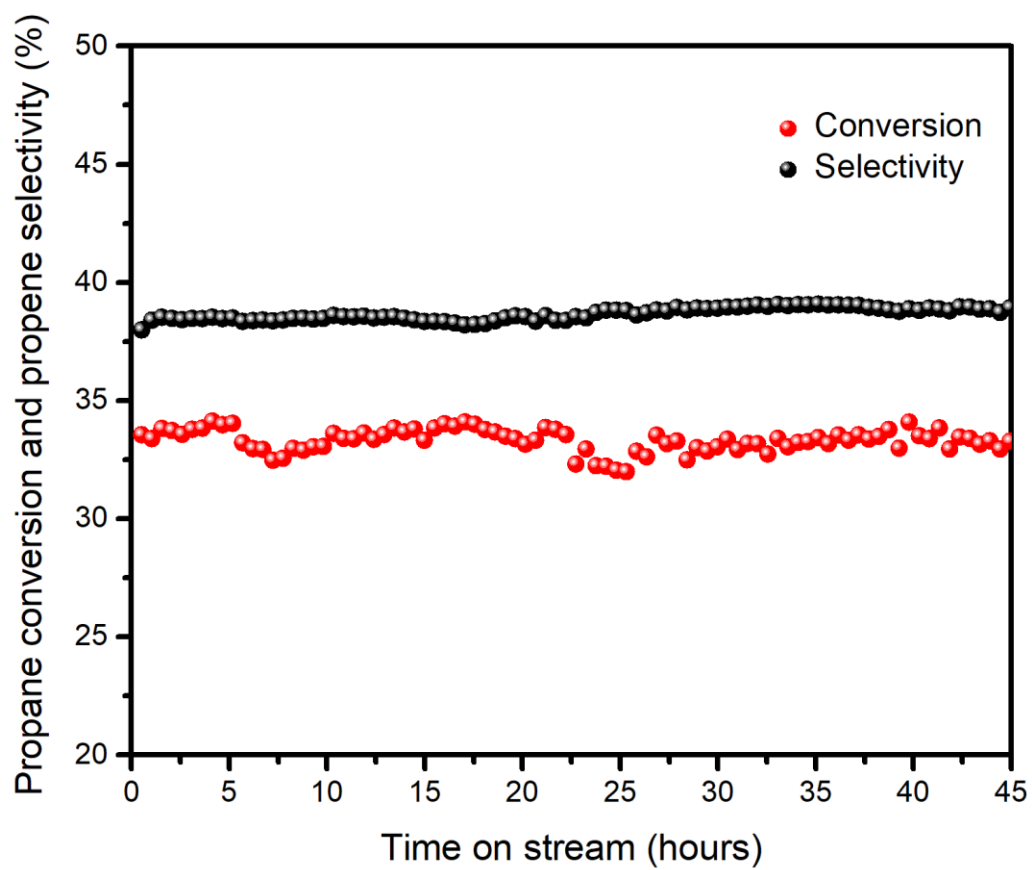
**Figure S7.** By-products distribution of propane dehydrogenation over  $\gamma\text{-Al}_2\text{O}_3\text{-100}$ .



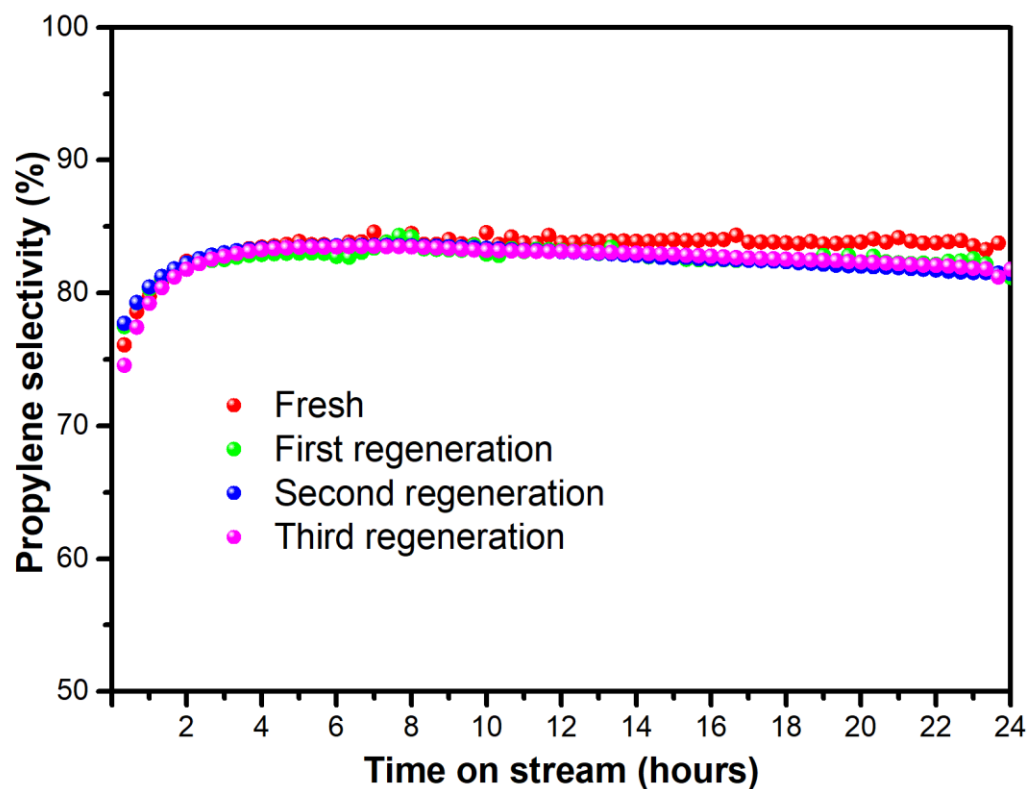
**Figure S8.** By-products distribution of propane dehydrogenation over  $\gamma\text{-Al}_2\text{O}_3\text{-200}$ .



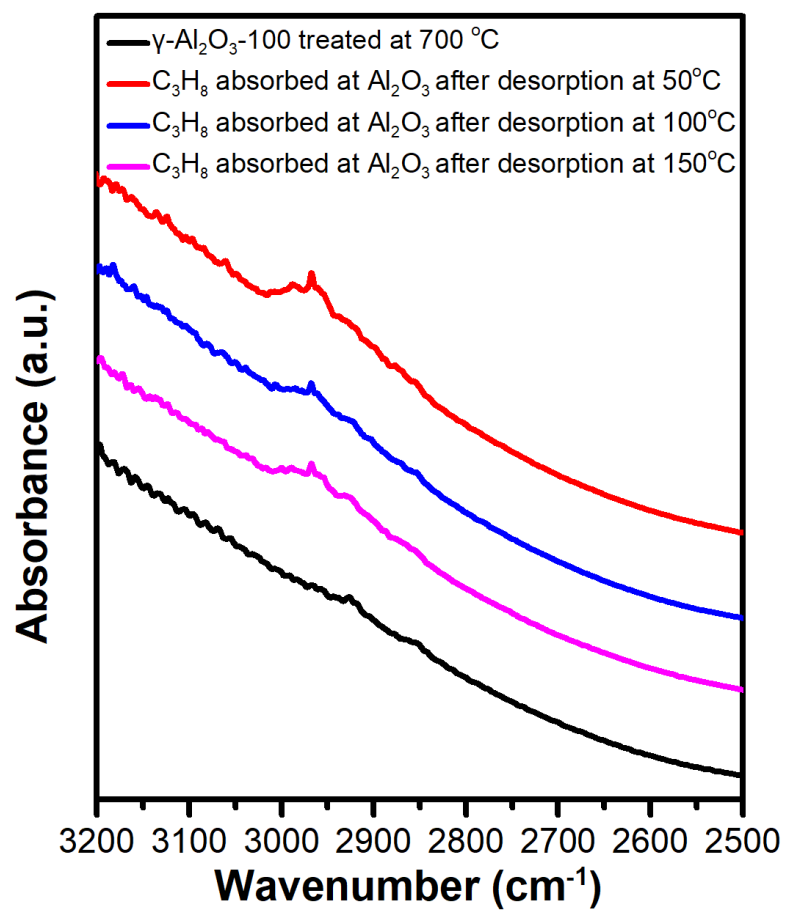
**Figure S9.** By-products distribution of propane dehydrogenation over  $\theta\text{-Al}_2\text{O}_3\text{-90}$ .



**Figure S10.** Catalytic performance of ZSM-5 in propane dehydrogenation reaction.

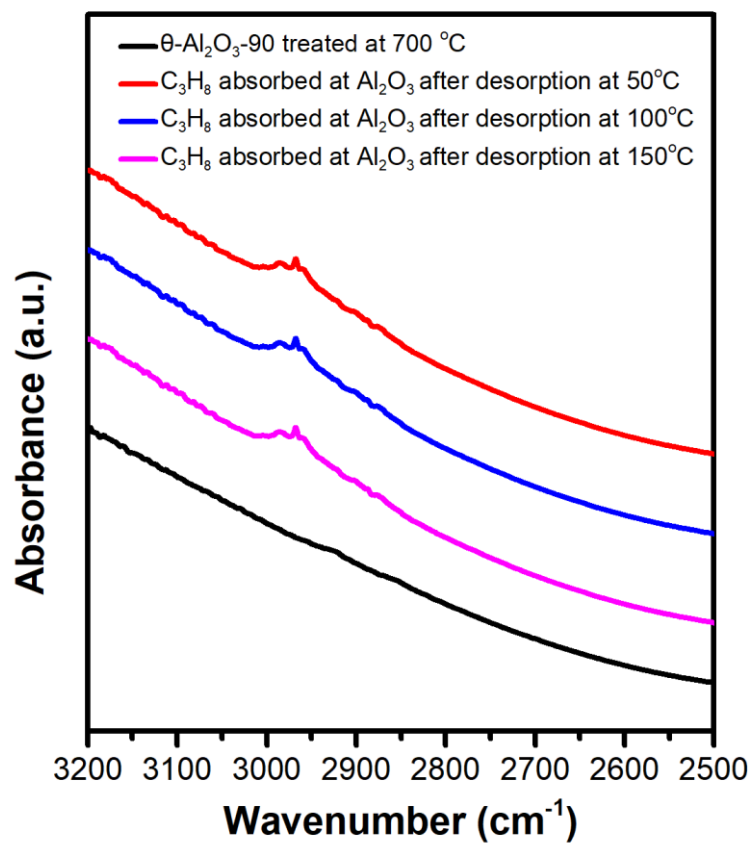


**Figure S11.** Propylene selectivity of propane dehydrogenation over the regenerated  $\gamma$ - $\text{Al}_2\text{O}_3$ -200 catalyst.



**Figure S12.** *in-situ* IR of propane adsorbed on  $\gamma$ - $\text{Al}_2\text{O}_3$ -100 catalyst.





**Figure S13.** *in-situ* IR of propane adsorbed on  $\theta$ - $\text{Al}_2\text{O}_3$ -90 catalyst.

**Table S1** Textural properties of different Al<sub>2</sub>O<sub>3</sub> catalysts.

Samples	S <sub>BET</sub> /(m <sup>2</sup> g <sup>-1</sup> )	V <sub>P</sub> /(cm <sup>3</sup> g <sup>-1</sup> )	D/nm
θ-Al <sub>2</sub> O <sub>3</sub> -90	95	0.56	10.39
γ-Al <sub>2</sub> O <sub>3</sub> -200	201	0.40	15.73
γ-Al <sub>2</sub> O <sub>3</sub> -100	102	0.43	31.67