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Electronic Supplementary Information for

Revealing fundamentals affecting activity and product selectivity in non-oxidative propane dehydrogenation over bare Al_2O_3

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Calculations of Mass Transport Limitations

Mears Criterion for External Diffusion Limitations

External diffusion limitations are negligible if

$$\frac{r_{obs} \cdot \rho_{catalyst} \cdot R \cdot n}{k_c \cdot C} < 0.15$$

r_{obs} – measured reaction rate, kmol/(kgcat·s)

$\rho_{catalyst}$ – catalyst density, kg/m^3

R – catalyst pellet radius, m

n – reaction order

k_c – mass transfer coefficient, m/s

C – bulk concentration of reactant, kmol/m^3

For propane dehydrogenation over the most active catalyst Al_2O_3_8.0 at 600°C with CO pretreatment:

$\frac{r_{obs} \cdot \rho_{catalyst} \cdot R \cdot n}{k_g \cdot C}$ = [$1.88 \cdot 10^{-5}$ kmol/(kg·s)]*[676 kg/m^3]·[$3.55 \cdot 10^{-4}$ m]*1/([$2.14 \cdot 10^{-1}$ m/s]·[$5.85 \cdot 10^{-3}$ kmol/m^3]) =0.0036 < 0.15

Weisz-Prater criterion for Internal Diffusion Limitations

To estimate the influence of internal diffusion on the reaction rates, we used Weisz-Prater criterion.

$$\Psi = \frac{n+1}{2} \cdot \frac{r \cdot \rho_{catalyst} \cdot R^2}{D \cdot C}$$

If $\Psi < 1$, internal diffusion limitations are negligible

n – reaction order

r_{obs} – measured reaction rate, kmol/(kgcat·s)

$\rho_{catalyst}$ – catalyst density, kg/m^3

R – catalyst pellet radius, m

D – diffusion coefficient, m^2/s

C – bulk concentration of reactant, kmol/m^3

For propane dehydrogenation over the most active catalyst Al_2O_3_8.0 at 600°C with CO pretreatment:

Ψ = [(1+1)/2] [$1.88 \cdot 10^{-5}$ kmol/(kgcat·s)]·[676 kg/m^3]·[$(3.55 \cdot 10^{-4})^2$ m^2]/([$1 \cdot 10^{-4}$ m^2/s]·[$5.85 \cdot 10^{-3}$ kmol/m3]) = 0.0027 < 1

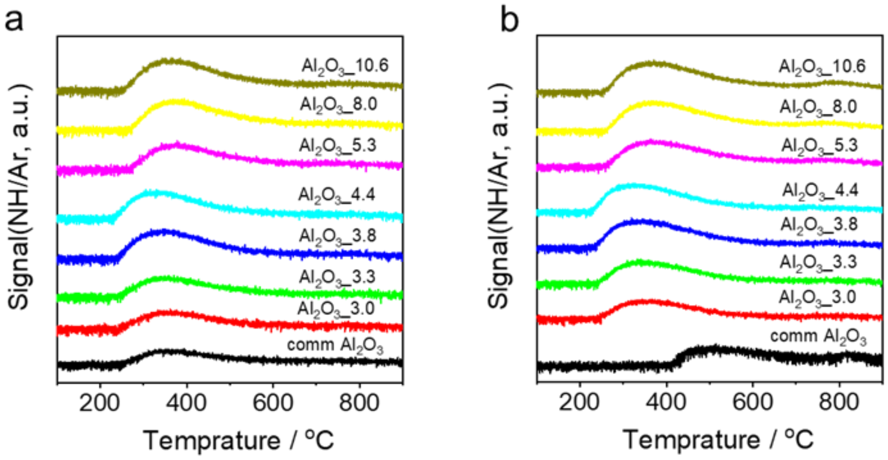

Figure S1 The NH_3-TPD profiles of commercial Al_2O_3 and in-house prepared Al_2O_3 samples aftre (a) H_2 or (b) CO treatment.

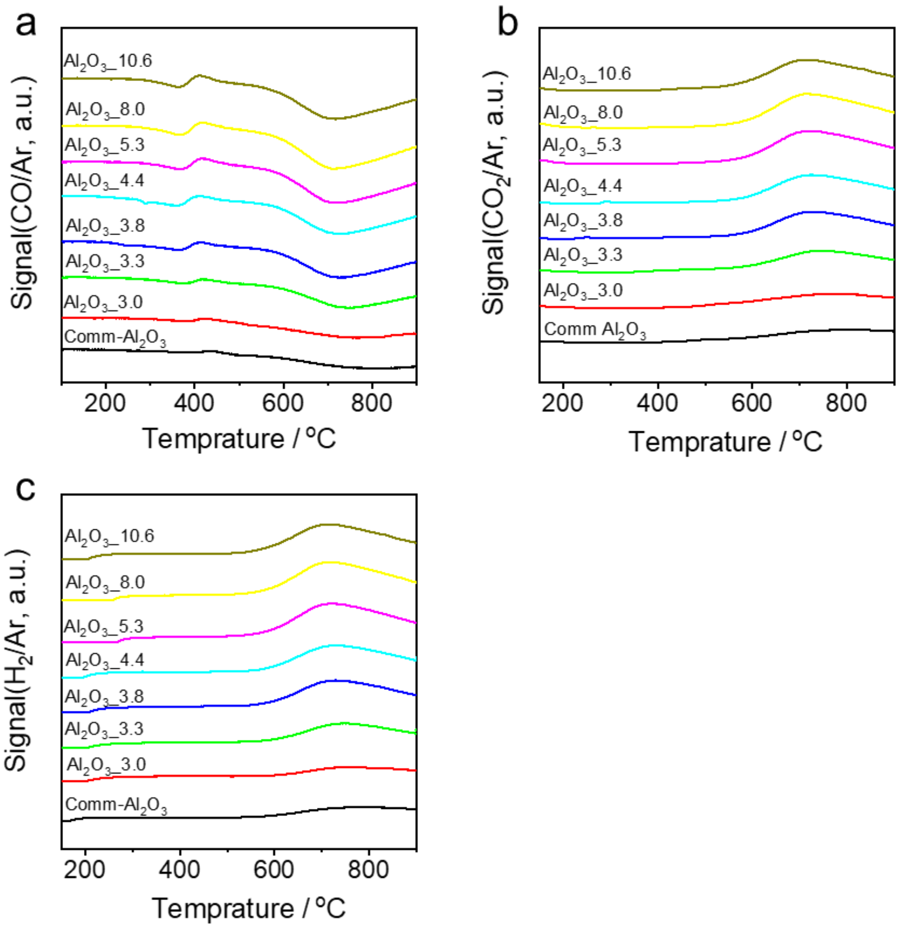

Figure S2 The MS signals (a) CO; (b) CO_2; (c) H_2 detected upon CO-TPR tests using differently prepared Al_2O_3 materials.

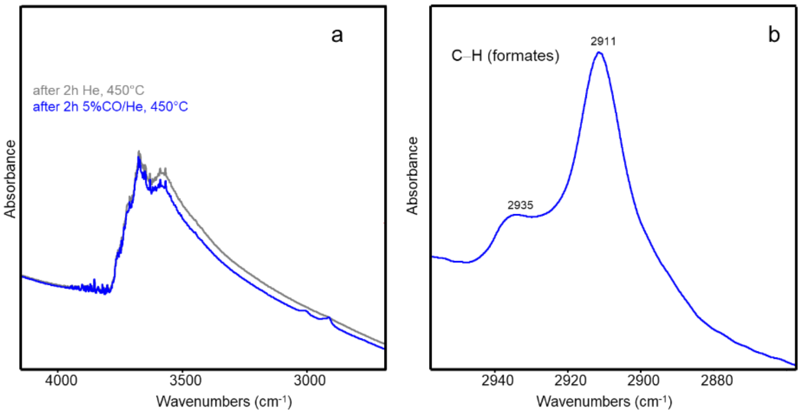

Figure S3 DRIFT spectra of Al_2O_3_8.0 in the (a) OH and (b) C-H stretch regions. The sample was pretreated in He at 450 °C for 2 h (grey line), and then exposed to 5 vol%CO in He for 2 h (blue line).

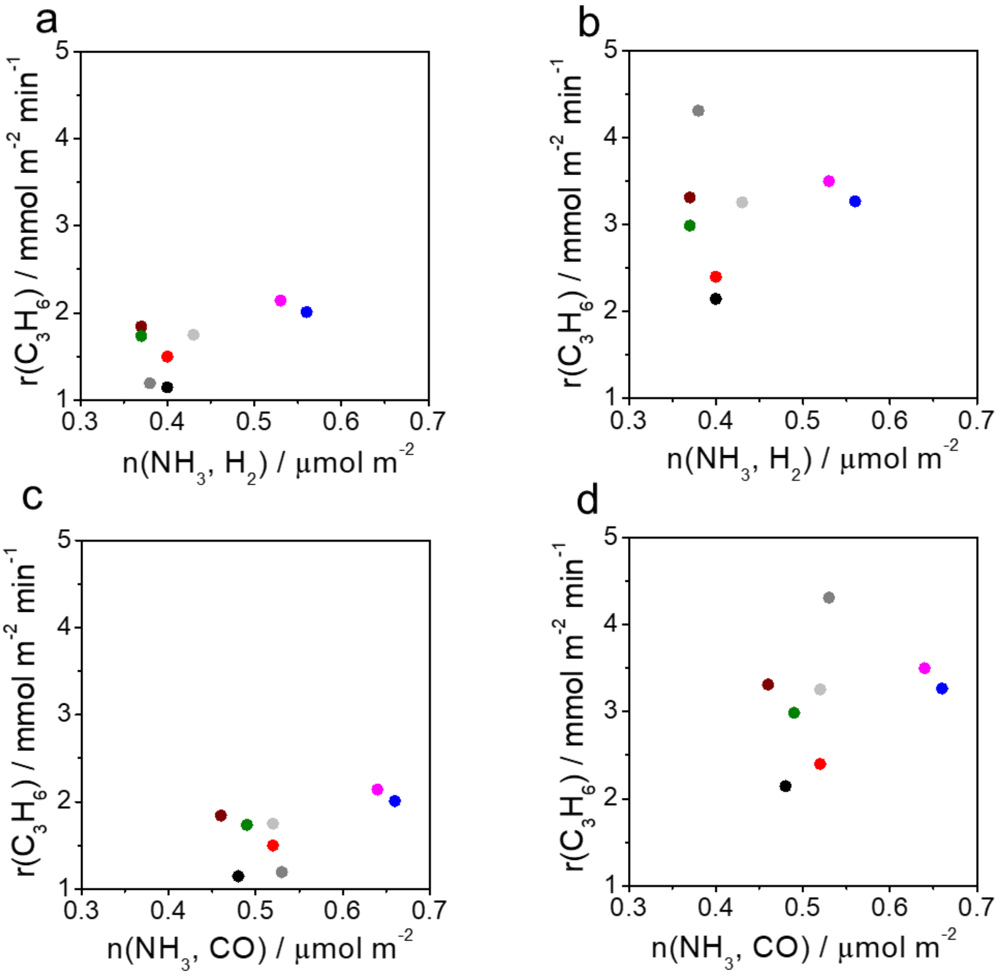

Figure S4 The rate of propene formation over samples treated in H_2 (a, b) or CO (c, d) as a function of the amount of NH_3 desorbed in NH_3-TPD tests with H_2- or CO-treated catalysts. ● - commercial Al_2O_3; ● - Al_2O_3_3.0; ● - Al_2O_3_3.3; ● - Al_2O_3_3.8; ● - Al_2O_3_4.4; ● - Al_2O_3_5.3; ● - Al_2O_3_8.0; ● - Al_2O_3_10.6. Reaction conditions: 600 °C, 50 mg catalysts, 40 ml/min, C_3H_8:N_2=2.3, WHSV(propane)=37.7 h^{-1}.

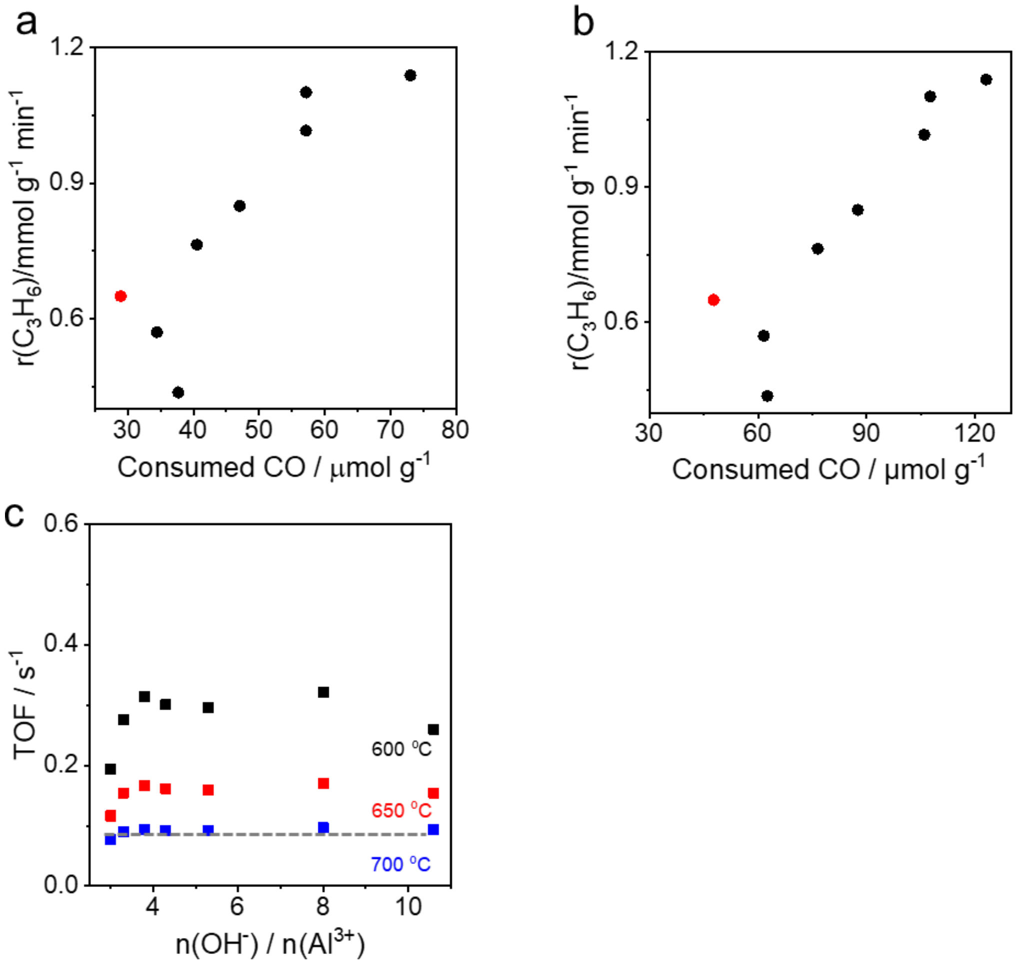

Figure S5 The rate of propene formation over samples treated in CO as a function of the amount of CO consumed up to (a) 600 °C and (b) 650 °C. (●) commercial Al_2O_3, (●) as-prepared Al_2O_3 samples. (c) the TOF values based on CO consumed up to 600, 650 or 700 °C upon CO-TPR as a function of molar ratio of OH^- and Al^{3+}.

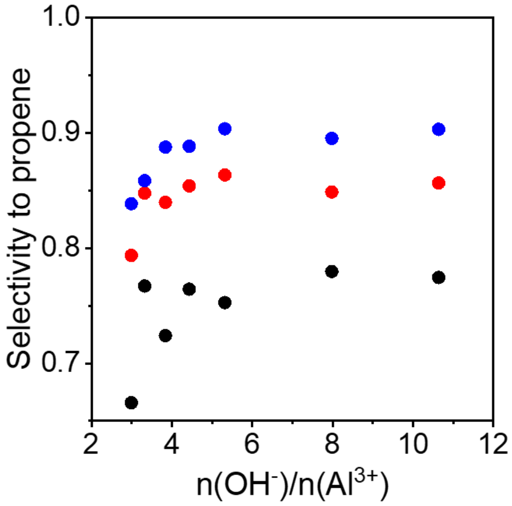

Figure S6 The selectivity to propene over non-treated (black), H_2-treated (red) or CO-treated (blue) Al_2O_3 samples.