Electronic Supplementary Information

Catalytic function of VO_x/Al_2O_3 for oxidative dehydrogenation of propane: support microstructure - dependent mass-transfer and diffusion

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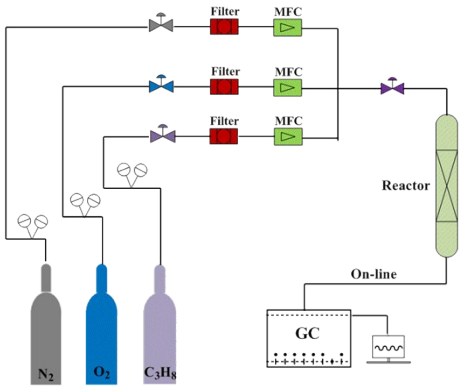
1 Experimental section

1.1 Catalytic assessment

Catalytic assessments of VO_x/Al_2O_3 catalysts in oxidative dehydrogenation of propane were performed using a lab-scale continue-flow fixed-bed reactor (stainless steel tubular of 8 mm i.d. and 300 mm length) at atmospheric pressure. The process flowchart is shown in Scheme. S1.



Scheme S1. Process flowchart toward oxidative dehydrogenation of propane reaction using continue-flow fixed-bed reactor

1.2 Definition

The relationship of carbon balance is shown in equation (S1), where $\boldsymbol{F_{in}}$ represents the flow-rate of feedstock, and pre-coefficient gives expression to carbon number of specific compounds, and $\boldsymbol{C}$ is the molar fraction, and $\boldsymbol{F_{out}}$ represents the flow-rate of effluents and is calculated by equation (S1).

$$F_{in} \times 3C_{in-C_3H_8} = F_{out} \times (3C_{out-C_3H_8} + C_{CO} + C_{CO_2} + C_{CH_4} + 2C_{C_2H_4} + 2C_{C_2H_6} + 3C_{C_3H_6}) \quad (S1)$$

The propane conversion and propylene selectivity were calculated by equation (S2) and (S3), respectively.

$$C_3H_8(Conversion)\% = \frac{F_{in-C_3H_8} - F_{out-C_3H_8}}{F_{in-C_3H_8}} \times 100\% \quad (S2)$$

$$C_3H_6(Selectivity)\% = \frac{F_{out} \times 3C_{C_3H_6}}{(F_{in-C_3H_8} - F_{out-C_3H_8}) \times 3} \times 100\% \quad (S3)$$

Surface density (***SD***) of catalysts is defined as the total number of V atoms per unit square nanometer. The specific calculation is based on equation (S4), where $\boldsymbol{x}$ is vanadium loading (5 wt.%), and $\boldsymbol{M}_v$ is standard atomic weight of vanadium (50.9), and $\boldsymbol{N}_A$ is Avogadro constant (6.02×10^{23}), and $\boldsymbol{S}_{BET}$ refers to the surface area of catalyst.

$$SD = \frac{x/M_V \times N_A}{S_{BET}} \quad (S4)$$

Weight hourly space velocity (***WHSV***, $g \cdot g^{-1} \cdot h^{-1}$) is defined as the quotient of the mass flow-rate of the propane divided by the mass of the catalyst ($\boldsymbol{w}_{cat}$) in the reactor at the condition of standard temperature and pressure (STP), as illustrated in equation (S5), where $\boldsymbol{V}_m$ is standard molar volume (22.4 mol/L).

$$WHSV = \frac{(F_{in-C_3H_8}/V_m) \times M_{C_3H_8}}{w_{cat}} \quad (S5)$$

The surface specific activity is expressed with turnover frequency ($TOF \times 10^{23}$), referring to mole of propane consumed per unit V-atom and per hour ($mol_{C3H8} \cdot V^{-1} \cdot h^{-1}$). The corresponding value is calculated by the equation S6, where ***SD*** is surface density.

$$TOF_{C_3H_8\ consuming} = \frac{(F_{in-C_3H_8}/V_m) \times C_3H_8(conversion)}{SD \times S_{BET} \times w_{cat}} \quad (S6)$$

Reaction rates (h^{-1}) are described as propane consuming and propylene formation rate, which refers to the total number of propane molecules consumed and total number of propylene molecules formed per unit V-atom and per hour, respectively. The specific calculation is based on equation S7 and S8, where $\boldsymbol{N}_A$ is Avogadro constant.

$$Rate_{C_3H_8\ consuming} = \frac{(F_{in-C_3H_8}/V_m) \times C_3H_8(conversion) \times N_A}{SD \times S_{BET} \times w_{cat}} = TOF_{C_3H_8\ consuming} \times N_A \quad (S7)$$

$$Rate_{C_3H_6\ formation} = \frac{(F_{in-C_3H_8}/V_m) \times C_3H_6(Yield) \times N_A}{SD \times S_{BET} \times w_{cat}} \quad (S8)$$

Space-time yield (***STY***, $g \cdot g^{-1} \cdot h^{-1}$) of propylene is defined to the weight of propylene per unit weight catalyst and per hour, and is calculated by the equation (S9).

$$STY = \frac{(F_{in-C_3H_8}/V_m) \times M_{C_3H_8}}{w_{cat}} \times C_3H_6(Yield) = WHSV \times C_3H_6(Yield) \quad (S9)$$

2 Results

2.1 Effect of calcination temperature on Al_2O_3 supports

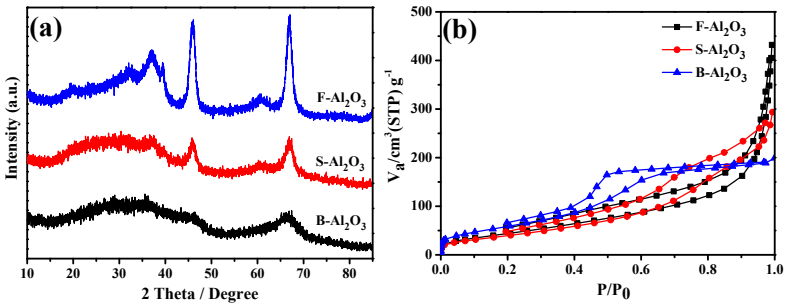


Fig. S1 Structural and textural characterization results of as-synthesized Al_2O_3 supports at calcination temperature of 550 °C, (a) XRD patterns and (b) N_2 adsorption-desorption isotherm curves

Table S1 Textural properties of as-synthesized Al_2O_3 supports at different calcination temperature

Supports	**Calcination temperature (°C)**	S_{BET} ($m^2 \cdot g^{-1}$)	V_{pore} ($cm^3 \cdot g^{-1}$)	D_{pore} (nm)
F-Al_2O_3-500	500	214	0.68	12.6
	550	175	0.64	14.6
S-Al_2O_3-500	500	150	0.36	9.6
	550	162	0.43	10.7
B-Al_2O_3-500	500	257	0.29	4.6
	550	242	0.30	5.0

To give a reliable explanation why the textural properties of catalysts are different from those of supports, we prepared all Al_2O_3 supports at calcination temperature of 550 °C. The resulting as-prepared Al_2O_3 supports were characterized by XRD and N_2 physical adsorption-desorption, as shown in Fig. S1. The corresponding surface area, pore size and volume were listed in Table S1. Compared with those Al_2O_3 supports prepared at 500 °C, it is found that increasing calcination temperature almost have no effect on crystalline structure of Al_2O_3 support, but has a slight effect on textural properties.

2.2 Product distribution and carbon balance

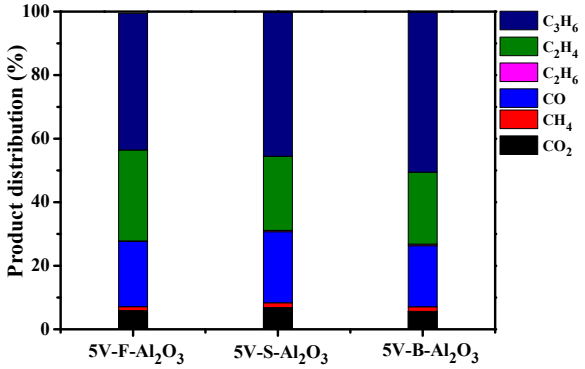


Fig. S2 Product distribution of ODHP reaction over 5V-M-Al_2O_3 catalysts, reaction condition: $\boldsymbol{m}_{cat}$=0.1 g, WHSV=9.43 $g \cdot g_{cat} \cdot h^{-1}$, ***T***=530 °C

2.3 Catalyst stability

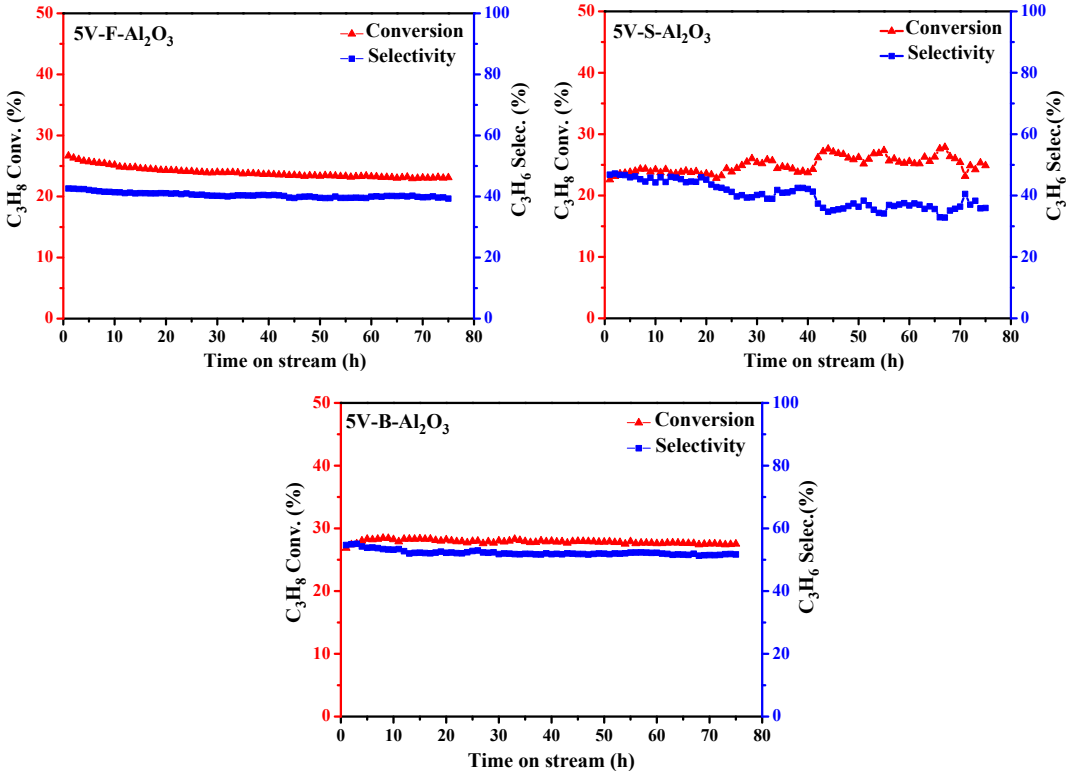


Fig. S3 Catalyst stability of 5V-M-Al_2O_3 catalysts for ODHP reaction, reaction condition: $\boldsymbol{m}_{cat}$=0.1 g, WHSV=9.43 $g \cdot g_{cat} \cdot h^{-1}$, ***T***=530 °C