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# Electronic Supporting Information

## Facilitating the Reduction of V-O Bonds on VO<sub>x</sub>/ZrO<sub>2</sub> Catalysts for Non-oxidative Propane Dehydrogenation

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## S1. Experimental and computational methods

#### **1.1 Characterization methods**

X-ray diffraction (XRD) measurements were performed on a Rigaku C/max-2500 diffractometer with CuKα radiation. Raman measurements of VZr with different loadings were conducted under ambient condition on a Renishaw inVia reflex Raman spectrometer equipped with visible (532 nm) Ar-ion laser beam. The samples were dried at 300 °C for 2 h before the measurement.

The measurement of specific surface area (SSA) of the samples was conducted on a Micromeritics Tristar 3000 analyzer at -196 °C. The Brunauer-Emmett-Teller (BET) method was applied to calculate SAAs on the basis of the N<sub>2</sub> isotherms.

H<sub>2</sub>-Temperature Program Reduction (H<sub>2</sub>-TPR) tests were executed on a Micromeritics AutoChem 2920 apparatus. The sample (0.4 g) was purged at 300 °C for one hour under an Ar stream (20 mL/min). After cooling down to 100 °C, H<sub>2</sub>-TPR was conducted in 10 vol % H<sub>2</sub>/Ar (30 mL/min) flow. The sample was headed up to 800 °C with a heating rate of 10 °C/min. The signal was detected with a thermal conductivity detector (TCD).

In situ Raman was performed on a Renishaw inVia reflex Raman spectrometer with 325 nm Ar-ion laser beam. The sample was pretreated with 1%  $O_2/N_2$  at 550 °C for 1 hour and recorded the signal. Then, the gas was changed to 10% H<sub>2</sub>/Ar and collected the spectra every minute.

XPS tests were executed on a PHI 1600 ESCA instrument (PE Company) equipped with an Al K $\alpha$  X-ray radiation source (hv = 1486.6 eV). Before the test, reduced samples were pretreated under H<sub>2</sub> atmosphere at 550 °C for 30 min. The binding energies were referenced to the C 1s peak at 284.6 eV.

#### 1.2 Reactivity test

Catalytic performance evaluation was carried out in a quartz fixed-bed reactor (8 mm ID) under 0.13 MPa. 0.4 g catalyst mixed with quartz sands were packed into the tube. The sample was heated up to 550 °C under N<sub>2</sub> flow (36 mL/min) and then reduced at the same temperature under H<sub>2</sub> atmosphere (H<sub>2</sub>:N<sub>2</sub>=7:36) for 30 minutes. Afterward, a mixture of C<sub>3</sub>H<sub>8</sub>, N<sub>2</sub> and H<sub>2</sub> (C<sub>3</sub>H<sub>8</sub>:N<sub>2</sub>:H<sub>2</sub>=7:36:7) was fed to the reactor at a rate of 50 mL/min. The products were analyzed with an online GC (2060) equipped with a flame ionization detector (Chromosorb 102 column) and a thermal conductivity detector (Al<sub>2</sub>O<sub>3</sub> Plot column). Propane conversion and propylene selectivity based on all products and gas-phase products were calculated from eq(1), eq(2) and eq(3).

Conversion (X) = 
$$\frac{F_{C_3H_8,in} - F_{C_3H_8,out}}{F_{C_3H_8,in}} \times 100\%$$
 (1)

Selectivity (S<sub>total</sub>) = 
$$\frac{F_{C_3H_6,out}}{F_{C_3H_8,in} - F_{C_3H_8,out}} \times 100\%$$
 (2)

Selectivity 
$$(S_{gas phase}) = \frac{3 \times F_{C_3H_6,out}}{\sum(n_i \times F_{i,out})} \times 100\%$$
 (3)

Where *i* stands for different carbon product in the gas phase.  $n_i$  stands for the number of carbon atom in the molecular.  $F_i$  stands for the molar flow rate of species *i*.

Turnover frequency (TOF) and propane conversion rates were determined under a special condition. Total flow rate was determined to eliminate the mass transfer and the conversion below 15% to ensure differential reaction. TOF was calculated based on the total number of V atom from eq(4).

$$TOF_{C_{3}H_{8}} = \frac{(F_{C_{3}H_{8},in} - F_{C_{3}H_{8},out}) \times N_{A}}{\text{total number of V atoms}}$$
(4)

As VOx could be well dispersed on ZrO2 as a monolayer, TOF based on the number of V atom will be same as

TOF based on active sites. This calculation method has been widely applied in many other works<sup>1-6</sup>. Nevertheless, for the catalysts with crystal V<sub>2</sub>O<sub>5</sub>, the calculated TOF would be smaller than the actual TOF based on the active sites.

#### 1.3 Models and computational details

Both VZr and VAI models and their correspond reduced models were created to investigate reducibility and propane dehydrogenation energy barriers. Monoclinic  $ZrO_2$  unit cell was cut along the ( $\overline{1}11$ ) plane and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> unit cell along the (100) plane to simulate surfaces of different supports. Results reported in this work use a p(2 x 2) m-ZrO<sub>2</sub> surface unit cell with four layers and p(1 x 2)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface unit cell with two Al-O-Al layers. The Brillouin zone was sampled using 2 x 2 x 1 k-points grid for VZr and 3 x 3 x 1 k-points grid for VAI. V<sub>2</sub>O<sub>5</sub> clusters with similar structures were added on these surfaces to represent VO<sub>x</sub> species. Three characteristic structures aimed to be compared were involved in these clusters: V=O, V-O-V and V-O-support.

Calculations were performed using Vienna ab initio simulation package (VASP)<sup>7, 8</sup>. In order to correct on site Coulomb correlation of occupied V 3d orbitals, we employed the gradient-corrected exchange-correlation functional by Perdew, Burke, and Ernzerhof (PBE)<sup>9</sup> and an effective Hubbard-type U parameter of 3.2 eV. The valence wave functions were expanded by plane wave with a cutoff energy of 400 eV. The atomic core was described by the Projected Augmented Wave (PAW) pseudopotentials<sup>10</sup>.

Due to the overbinding of GGA in the  $O_2$  molecule, we used  $H_2(g)$  and  $H_2O(g)$  as reference for oxygen vacancy formation energy:

$$\Delta E_{\rm V} = E_{\rm surface \ with \ Ov} + E_{\rm H_2O(g)} - E_{\rm clean \ surface} - E_{\rm H_2(g)}$$
(5)

In potential energy diagrams, the energy of  $C_3H_8$  in the gas phase is taken as reference and the energy of intermediates are corrected with  $H_2$  in the gas phase. The adsorption energy is defined as:

$$\Delta E_{ads} = E_{C_3H_x + surface} + \left[\frac{8-x}{2}\right] E_{H_2(g)} - E_{clean surface} - E_{C_3H_8(g)}$$
(6)

Moreover, the transition states were located by the climbing-image nudged elastic band method (NEB)<sup>11</sup>. The activation barrier E<sub>a</sub> was calculated based on following equation:

$$\Delta E_{a} = E_{\text{transition state}} - E_{\text{initial state}}$$
(7)

# S2. Supporting tables and figures

## 2.1 Supporting tables

aispersion states.						
V loading	BET surface	V density	Type of VO <sub>x</sub> formed*			
(wt.%)	area (m²/g)	(nm⁻¹)				
0.2	48.6	0.49	Sub-monolayer			
0.5	50.7	1.2	Sub-monolayer			
1	48.2	2.5	Sub-monolayer			
1.5	47.9	3.7	Sub-monolayer			
2	47.0	5.0	Actual monolayer without $V_2O_5$			
2.5	42.9	6.9	Theoretical monolayer.			
			Little V <sub>2</sub> O <sub>5</sub>			
3	42.4	8.4	Monolayer VO <sub>x</sub> & V <sub>2</sub> O <sub>5</sub>			
4	40.6	11.6	Monolayer VO <sub>x</sub> & V <sub>2</sub> O <sub>5</sub>			
	V loading (wt.%) 0.2 0.5 1 1.5 2 2.5 3 4	V loading BET surface   (wt.%) area (m²/g)   0.2 48.6   0.5 50.7   1 48.2   1.5 47.9   2 47.0   2.5 42.9   3 42.4   4 40.6	V loading BET surface V density   (wt.%) area (m²/g) (nm⁻¹)   0.2 48.6 0.49   0.5 50.7 1.2   1 48.2 2.5   1.5 47.9 3.7   2 47.0 5.0   2.5 42.9 6.9   3 42.4 8.4   4 40.6 11.6			

Table S1. Catalysts and their V loadings ( $\omega$ (V)), BET surface areas (S<sub>BET</sub>), V surface densities and dispersion states.

\*Type of VO<sub>x</sub> formed is determined by vis-Raman spectra.

Talacs.						
Sample	V surface density	r(C <sub>3</sub> H <sub>8</sub> )	*TOF /s <sup>-1</sup>			
	/nm <sup>-2</sup>	/ mmol·g <sup>-1</sup> ·min <sup>-1</sup>				
ZrO <sub>2</sub>	—	0.03	—			
0.2VZr	0.49	0.048	0.0204			
0.5VZr	1.2	0.089	0.0151			
1VZr	2.5	0.205	0.0174			
1.5VZr	3.7	0.265	0.0159			
2VZr	5.0	0.312	0.0132			
1VAI	0.6	0.032	0.0025			
6VAI	4.0	0.121	0.0017			

Table S2. Catalysts and their V surface densities, initial rates of C<sub>3</sub>H<sub>8</sub> consumption (r(C<sub>3</sub>H<sub>8</sub>)) and TOF values.

\* TOF is calculated based on the number of V atoms.

Sample	H: V*	AOS of V*
1VZr	1.5	3.5
1VAI	1.0	4.0
ZrO <sub>2</sub>	-	-

Table S3. Numbers of H atoms consumption per V atom and average oxidation state of V.

\*Calculated from H<sub>2</sub>-TPR result.

	BE of	BE of	V	/3+	V	4+	V	/5+
Sample	lattice	adsorbed	BE	Area	BE	Area	BE	Area
Campio	oxygen	oxygen		(0/)		(0/)		(0/)
	O <sub>I</sub> (eV)	O⊫(eV)	(ev)	(%)	(ev)	(%)	(ev)	(%)
1VAI	531.1	532.3	515.8	6.2	516.8	40.1	517.8	53.7
1VZr	529.6	531.2	515.8	58.2	516.8	35.3	517.8	6.5

Table S4. XPS results and deconvolution results of V 2p<sub>3/2</sub>.

Catalysts	Temperature (°C)	WHSV (h <sup>-1</sup> )	TOF (h <sup>-1</sup> )	References
1VZr	550	2.07	57.6	This work
1VAI	550	2.07	9.6	This work
isolated Ga/SiO <sub>2</sub>	550	0.33	20.0	Chem. Sci., 2017, 8, 2661-2666
Ga(i-Bu) <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	550	1.48	27.2 <sup>*</sup>	ACS Catal. 2018, 8, 7566-7577
Ga(i-Bu) 3/SiO2	550	2.36	11.2 <sup>*</sup>	ACS Catal. 2018, 8, 7566-7577
islated Fe/SiO <sub>2</sub>	650	0.39	1.4	ACS Catal. 2015, 5, 3494-3503
isolated Cr/SiO <sub>2</sub>	550		10.3	Inorg. Chem. 2015, 54, 11, 5065- 5078
isolated Cr/Al <sub>2</sub> O <sub>3</sub>	550		60.0	Organometallics 2017, 36, 1, 234- 244
isolated Co/SiO <sub>2</sub>	550	0.076	12.6	J. Catal. 2015, 322, 24-37
isolated V/SiO <sub>2</sub>	500	0.12	1.66*	Organometallics 2013, 32, 21, 6452- 6460

Table S5. Comparation of catalytic performance in this work with previous works.

\* TOF calculated from given data.

## 2.2 Supporting figures



Figure S1. (a) XRD patterns and (b) vis-Raman spectra of VZr catalysts with different V loadings.



**Figure S2**. (a) Gas phase selectivity of 1VAI, 1VZr and  $ZrO_2$ . Reaction condition:  $m_{cat}=0.4$  g;  $C_3H_8:N_2:H_2 = 7:36:7$ ; T = 550 °C; inlet flow = 50 mL/min. (b) Propane conversion and propene total selectivity of 1VZr, 1VAI and  $ZrO_2$ .



**Figure S3**. Propane conversion and selectivity of 1VZr during reaction-regeneration cycles. Reaction condition:  $m_{cat} = 0.4 \text{ g}$ ;  $C_3H_8:N_2:H_2 = 7:36:7$ ; T = 550 °C; inlet flow = 50 mL/min



**Figure S4**.  $C_3H_8$ -TPSR of 3VAI. Propane: m/e = 29. Propene: m/e = 41. H<sub>2</sub>: m/e = 2.



Figure S5. XPS Zr 3d peaks of reduced  $ZrO_2$  and 1VZr.



**Figure S6**. H<sub>2</sub>-TPR profiles of VZr and VAI with a series of V loadings. The signal of VZr catalysts are 4 times amplified.



**Figure S7.** (a) Top- and (b) side-view of dimeric  $V_2O_5$  supported on m-ZrO<sub>2</sub>( $\overline{1}11$ ). (c) Top- and (d) side-view of dimeric  $V_2O_5$  supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100). Color scheme: V gray; O red; Zr cyan; Al purple.



Figure S8. XPS (a) C 1S (b) O 1s peaks of 1VZr and 1VAI after 30 mins reduction.

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