Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Revealing the mechanism of $VO_x/Ti_3AlC_2$ for the dehydrogenation of propane

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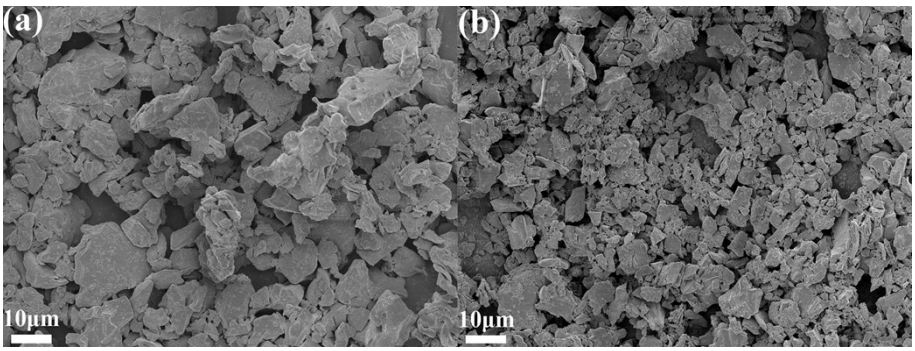


**Fig. S1** SEM images for $Ti_3AlC_2$ (a) and $1.2V/Ti_3AlC_2$ (b).

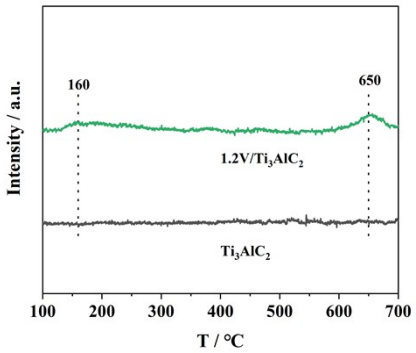


**Fig. S2** $NH_3$-TPD profiles of $Ti_3AlC_2$ and supported $VO_x/Ti_3AlC_2$ catalysts.

Table S1 Analysis of V 2p of $xV/Ti_3AlC_2$ catalysts

| Samples | Peak area fractions (%) | |
|---|---|---|
| | $V^{4+}$ (516.6 eV) | $V^{5+}$ (517.6 eV) |
| $0.2V/Ti_3AlC_2$ | 59.0 | 41.0 |
| $1.2V/Ti_3AlC_2$ | 34.3 | 65.7 |
| $2.4V/Ti_3AlC_2$ | 25.1 | 74.9 |
| $4.1V/Ti_3AlC_2$ | 11.2 | 88.8 |

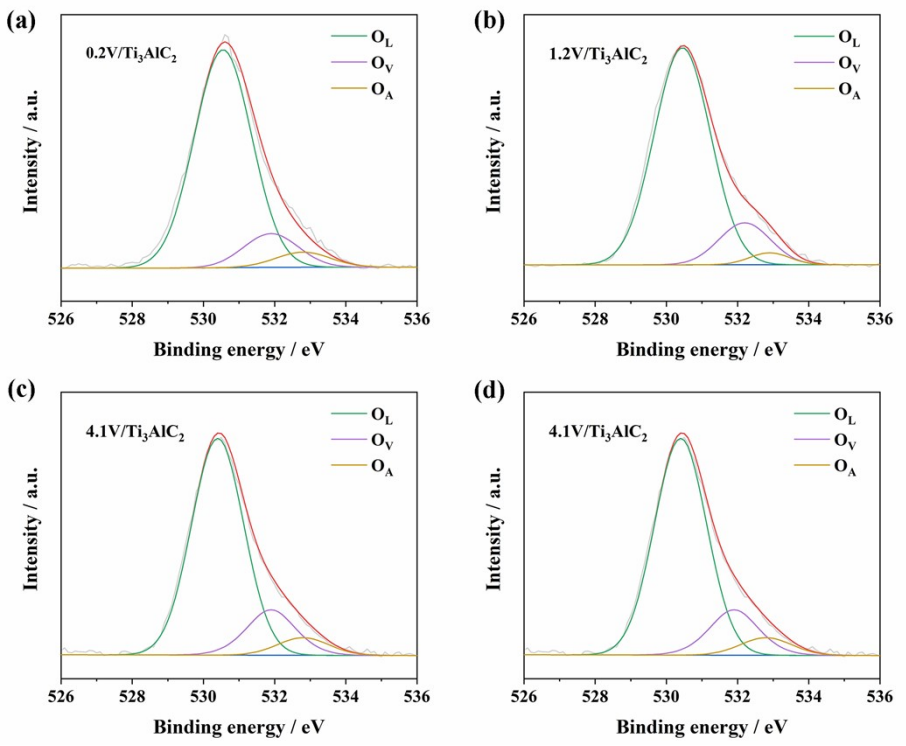


**Fig. S3** O 1s XPS spectra of 0.2-4.1V/$Ti_3AlC_2$.

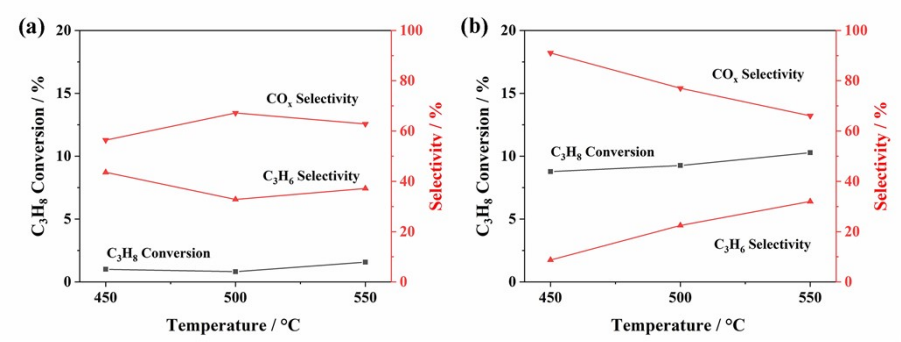


**Fig. S4** The ODHP performance of $Ti_3AlC_2$ (a) and $Ti_3AlC_2$ calcined at 550 °C in air (b). Reaction conditions: $m_{cat}$ = 1.0g, T=450-550 °C, $C_3H_8$/Air=1: 1.2, inlet flow = 8.8 ml $min^{-1}$.

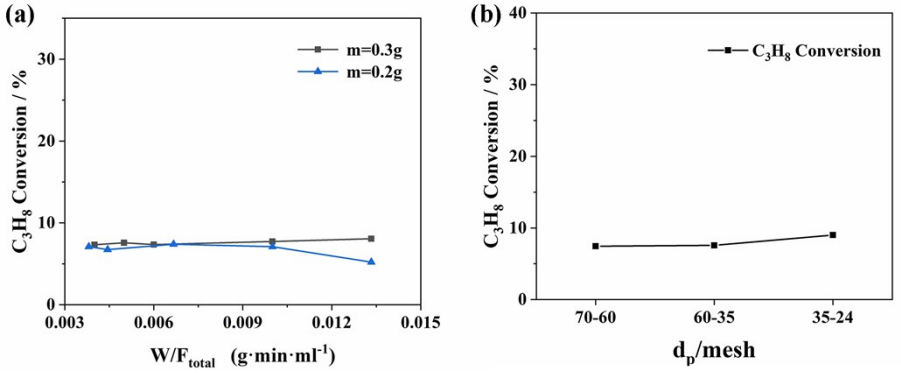


**Fig. S5** The influence of contact time (a) and catalyst particle size (b) on the $C_3H_8$ conversion at 500 °C.

0.2 and 0.3 g 1.2V/$Ti_3AlC_2$ catalyst diluted with quartz sand were placed in a fixed bed to investigate to external diffusion influence. $C_3H_8$ conversion is almost same on the catalysts with different mass in the range of total space velocity of 6000-15750 ml $h^{-1}$ $g_{cat}^{-1}$ (Figure S4(a)), suggesting that there is no effect of external diffusion. In addition, at a total space velocity of 12000 ml $h^{-1}$ $g_{cat}^{-1}$, $C_3H_8$ conversion is similar in the range of catalyst particle size of 35-60 mesh (Figure S4(b)), which is the characteristic of internal diffusion exclusion.

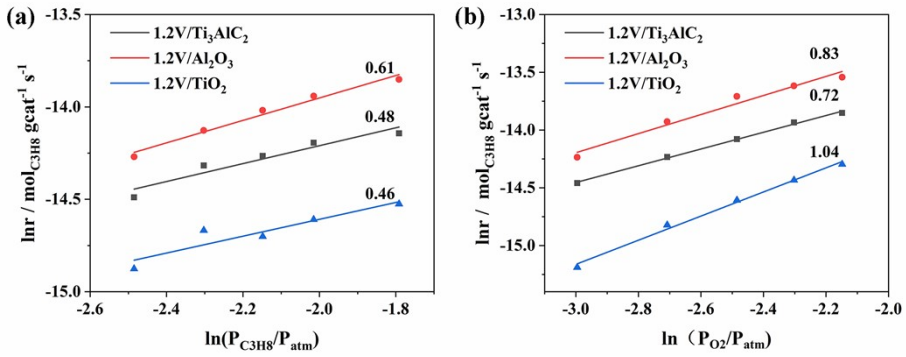


**Fig. S6** Dependence of $(x_{C_3H_8} x_{O_2}/r)^{1/2}$ on $x_{C_3H_8}$ (a) and $x_{O_2}$ (b) in the range of $x_{C_3H_8}$ = 0.083-0.167 and $x_{O_2}$= 0.067-0.133.

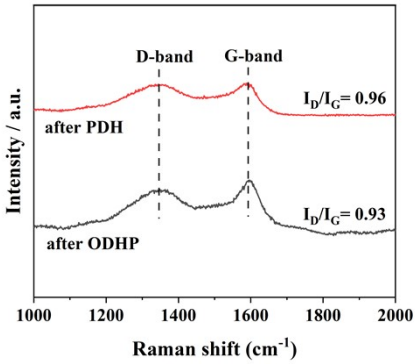


**Fig. S7** Raman spectra for the spent 1.2V/$Ti_3AlC_2$ catalysts after 2h reaction. Reaction conditions: ODHP reaction, $m_{cat}$ = 1.0 g, $C_3H_8$/Air=1: 1.2 ($C_3H_8$: $O_2$ = 1: 0.25), inlet flow = 8.8 ml $min^{-1}$; PDH reaction, $m_{cat}$ = 1.0 g, $C_3H_8/N_2$=1: 1.2, inlet flow = 8.8 ml $min^{-1}$.

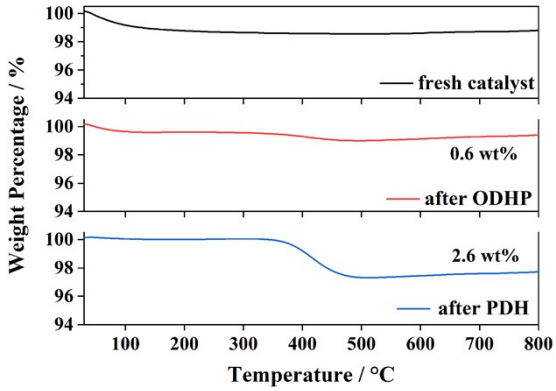


**Fig. S8** TGA curves for the fresh 1.2V/$Ti_3AlC_2$ catalyst and the spent 1.2V/$Ti_3AlC_2$ catalysts after 2h reaction. Reaction conditions: ODHP reaction, $m_{cat}$ = 1.0 g, $C_3H_8$/Air=1: 1.2 ($C_3H_8$: $O_2$ = 1: 0.25), inlet flow = 8.8 ml $min^{-1}$; PDH reaction, $m_{cat}$ = 1.0 g, $C_3H_8/N_2$=1: 1.2, inlet flow = 8.8 ml $min^{-1}$.

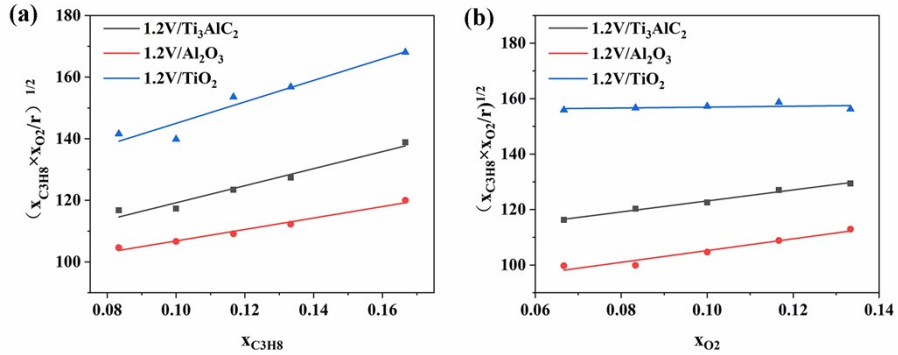


**Fig. S9** Dependence of reaction rates on the partial pressure of (a) propane (8.3-16.7 kPa) and (b) oxygen (5-11.7 kPa) over different catalysts in ODHP reaction. The reactions were carried out at 500 °C and the total space velocity is 12000 mL $h^{-1}$ $g_{cata}^{-1}$.

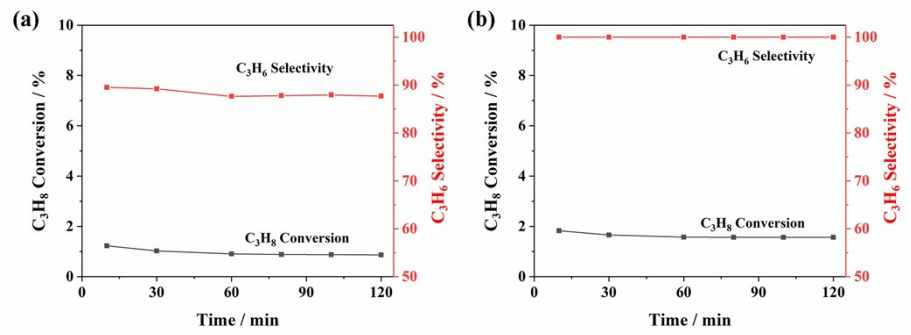


**Fig. S10** The PDH performance of $Ti_3AlC_2$ (a) and $Ti_3AlC_2$ calcined at 550 °C in air (b). Reaction conditions: $m_{cat}$ = 1.0g, T=550 °C, $C_3H_8/N_2$=1: 4, inlet flow = 20 ml $min^{-1}$.

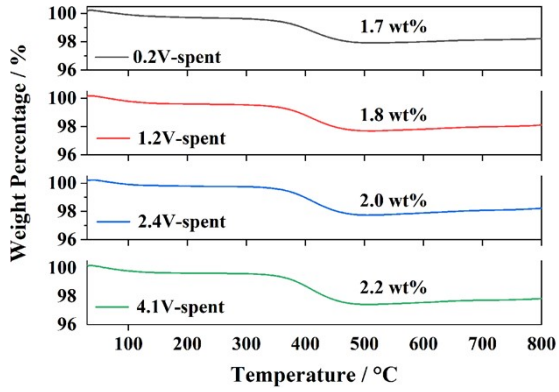


**Fig. S11** TGA curves for the spent catalysts after 2h reaction. Reaction conditions: $m_{cat}$ = 1.0 g, T=550 °C, $C_3H_8/N_2$=1: 4, inlet flow = 20 ml $min^{-1}$.

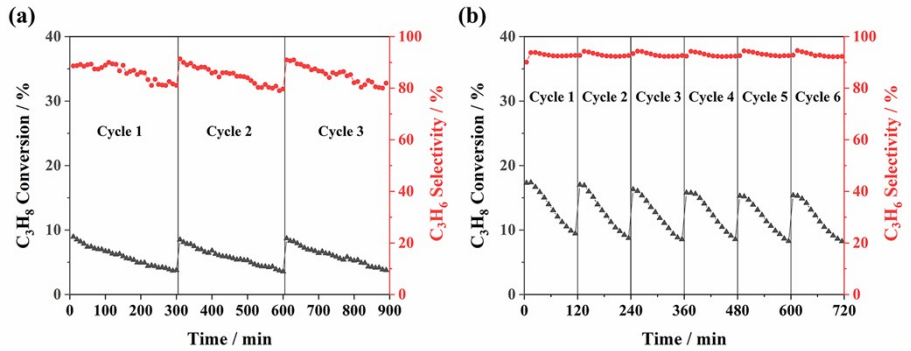


**Fig. S12** The catalytic performance of 1.2V/$Ti_3AlC_2$ catalyst in ODHP (a) and PDH (b) reactions as a function of time. Reaction conditions: ODHP reaction, T=550 °C, $m_{cat}$ = 1.0 g, $C_3H_8$/Air=1: 1.2 ($C_3H_8$: $O_2$ = 1: 0.25), inlet flow = 8.8 ml $min^{-1}$; PDH reaction, T=550 °C, $m_{cat}$ = 1.0 g, $C_3H_8/N_2$=1: 4, inlet flow = 20 ml $min^{-1}$.

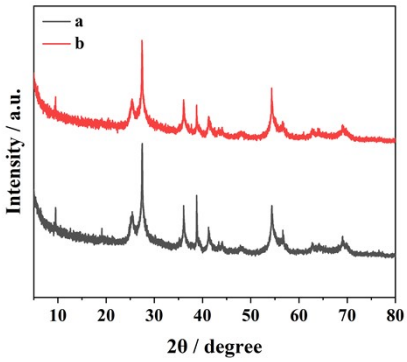


**Fig. S13** XRD patterns of the 1.2V/$Ti_3AlC_2$ catalysts after ODHP (a) and PDH (b) regenerative cycles.

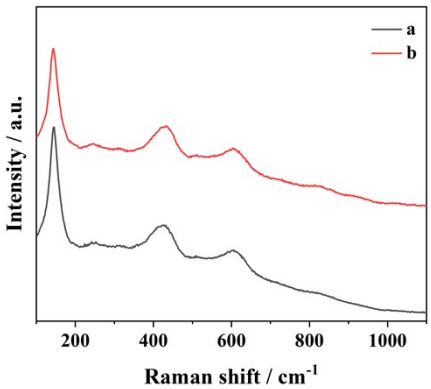


**Fig. S14** Raman spectra of the 1.2V/$Ti_3AlC_2$ catalysts after ODHP (a) and PDH (b) regenerative cycles.

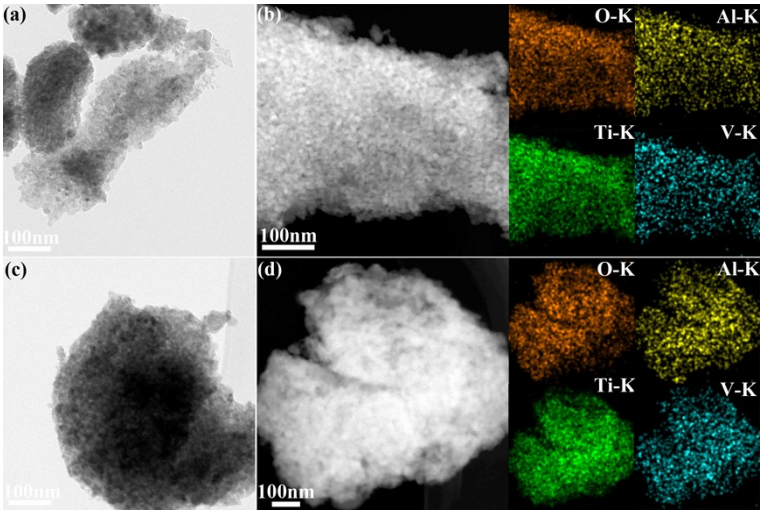


**Fig. S15** TEM images and EDS mapping for 1.2V/$Ti_3AlC_2$ catalysts after ODHP (a, b) and PDH (c, d) regenerative cycles.