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#### Broader context

Although the oxidative dehydrogenation of propane with carbon dioxide ( $CO_2$ -ODP) is a sustainable route for the efficient production of propene in tandem with  $CO_2$  reduction to CO, the rational design of high-performance catalysts for this green process is challenged by limited understanding of the nature of active sites and the reaction mechanism. Supported vanadium oxides ( $VO_x$ ) are promising for  $CO_2$ -ODP considering their low price, environmental sustainability, and competitive catalytic performance, however the essential reason of  $VO_x$  structural effects on the catalytic performance is still ambiguous from a mechanistic aspect. In present work,  $SiO_2$ -supported  $VO_x$  catalysts with narrow distributions of V loading while well-defined structures of  $VO_x$  species, *i.e.*, monomeric  $VO_x$ , less polymeric  $VO_x$ , highly polymeric  $VO_x$  and  $V_2O_5$  crystallites, were on-purpose synthesized. In addition to sophisticated catalytic tests for  $CO_2$ -ODP, complementary characterization techniques were applied for deriving structural and mechanistic insights into catalyst functioning. We established that the catalytic activity and stability of different  $VO_x$  species coincide well with the ability for the re-oxidation of correspondingly reduced  $VO_x$  by  $CO_2$ . These findings are important guidelines for purposeful development of efficient supported  $VO_x$  catalysts for  $CO_2$ -ODP.

be guidelines for developing a high-performance  $VO_x$ -based catalyst for  $CO_2$ -ODP.

Bridging the structural gap of supported

propane with carbon dioxide<sup>†</sup>

vanadium oxides for oxidative dehydrogenation of

Li Wang,<sup>ab</sup> Heng-Bo Zhang,<sup>a</sup> Rongrong Hu, D<sup>a</sup> Han-Qing Ge,<sup>a</sup> Yong-Hong Song,<sup>a</sup>

As an extensively used industrial catalyst for oxidation reactions, supported vanadium oxide (VO<sub>x</sub>) is a promising candidate for oxidative dehydrogenation of propane with carbon dioxide (CO<sub>2</sub>-ODP). Although the structure of VO<sub>x</sub> is found to be a key factor in determining the catalytic activity and stability of supported VO<sub>x</sub> for CO<sub>2</sub>-ODP, the essential reason still remains elusive at the molecular level. To shed some light on this fundamental issue,  $VO_x/(-)SiO_2$  catalysts with narrow distributions of V loading while well-defined structures of VO<sub>x</sub> species, *i.e.*, monomeric VO<sub>x</sub>, less polymeric VO<sub>x</sub>, highly polymeric VO<sub>x</sub> and V<sub>2</sub>O<sub>5</sub> crystallites, were purposely synthesized by appropriate methods, including one-pot hydrothermal synthesis, incipient wetness impregnation and physical grinding. We found that the catalytic activity and stability of VO<sub>x</sub> species decrease in the order of monomeric VO<sub>x</sub> > less polymeric VO<sub>x</sub> > highly polymeric VO<sub>x</sub> > highly polymeric VO<sub>x</sub> species by CO<sub>2</sub>, which coincides with the ability for the re-oxidation of the reduced VO<sub>x</sub> species by CO<sub>2</sub>. As a result of the most facile re-oxidation of the reduced

monomeric VO<sub>x</sub> species by CO<sub>2</sub>, a well matched redox cycle of  $V^{5+}/V^{4+}$  oxides during CO<sub>2</sub>-ODP can be maintained with increasing the time on stream, leading to an improved stability of the catalyst with more

monomeric VO<sub>x</sub>. These mechanistic findings on the redox properties of VO<sub>x</sub> with different structures can

Guo-Qing Yang,\*<sup>a</sup> Yuefeng Li,<sup>b</sup> Zhao-Tie Liu<sup>b</sup> and Zhong-Wen Liu<sup>\*</sup>

### 1. Introduction

Among the currently available methods, the production of propene from propane through either the direct dehydrogenation or the oxidative dehydrogenation reaction is the most competitively favorable route.<sup>1,2</sup> However, only the direct propane dehydrogenation (PDH) technologies are commercialized on large scales, which characterize low propene productivity and high energy consumption.<sup>2,3</sup> To overcome these shortcomings, the oxidative dehydrogenation of propane using carbon dioxide as a soft oxidant (CO<sub>2</sub>-ODP) has attracted much attention.<sup>3,4</sup> In comparison with PDH, CO<sub>2</sub>-ODP can promote the equilibrium conversion of propane by removing the produced hydrogen *via* CO<sub>2</sub> reduction. Moreover, CO<sub>2</sub>-ODP favors a higher propene selectivity than that by using O<sub>2</sub> as an oxidant due to the soft oxidizing

<sup>&</sup>lt;sup>a</sup> Key Laboratory of Syngas Conversion of Shaanxi Province, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China.

E-mail: gqyang@snnu.edu.cn, zwliu@snnu.edu.cn

<sup>&</sup>lt;sup>b</sup> Kaili Catalyst & New Materials Co., Ltd, Xi'an 710201, China

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ability of CO<sub>2</sub>. Importantly, the efficient production of two valueadded products of propene and CO from propane and the greenhouse gas of CO<sub>2</sub>, respectively, turns CO<sub>2</sub>-ODP into a charming tandem process from an environmental viewpoint.4,5 Moreover, although the separation of gaseous species resulting from the introduction of CO<sub>2</sub> remains a significant challenge, the CO<sub>2</sub>-ODP product mixtures can be directly used as feeds to produce useful chemicals, such as the oxidative coupling of CO<sub>2</sub> with alkenes to produce acrylic acids and acrylate in a one-step process, which is a more energy-saving and efficient technology than the conventional two-step methodology.<sup>6</sup> As a result of these advantages, a number of catalysts including supported or bulk metal oxides e.g., Cr,<sup>7</sup> V,<sup>8</sup> In,<sup>9</sup> Ga,<sup>10</sup> and Zn,<sup>11</sup> and supported metals, *e.g.*, Pd,<sup>12</sup> and Pt<sup>13,14</sup> have been extensively studied for CO<sub>2</sub>-ODP. Among these potential catalysts, supported vanadium oxides (VO<sub>x</sub>) are promising for CO<sub>2</sub>-ODP considering their low price, environmental sustainability and competitive catalytic performance.<sup>2,15</sup> However, the rational design of a high-performance supported VO<sub>x</sub> catalyst is still challenging due to limited understanding of the active and stable nature of  $VO_x$  species as well as the reaction mechanism.

Indeed, the apparent turnover frequency (TOF) of the supported  $VO_x$  for activating propane during  $CO_2$ -ODP has been revealed to be decreased with increasing the polymerization degree of VO<sub>x</sub> species.<sup>16,17</sup> A similar conclusion is also valid for the oxidative dehydrogenation of ethylbenzene with CO<sub>2</sub> reaction, in which monomeric VO<sub>x</sub> are more active and more stable than polymeric VO<sub>x</sub> and crystalline V<sub>2</sub>O<sub>5</sub>.<sup>18</sup> Although these observations are tentatively correlated with the structural and chemical properties of VO<sub>x</sub> species with different structures, the essential reason in the mechanistic aspect, especially the activation of CO<sub>2</sub> and the balance between the activations of C-O bonds in CO<sub>2</sub> and C-H bonds in C<sub>3</sub>H<sub>8</sub> molecules, is still ambiguous. In the cases of the reducible metal oxide catalysts, e.g.,  $CrO_x$  and  $VO_x$ , the  $CO_2$ -ODP reaction may follow the Marsvan-Krevelen redox mechanism.<sup>8,19</sup> Thus, the redox cycles of the VO<sub>x</sub> species participated with CO<sub>2</sub> and propane must proceed quickly in a well-matched manner, which is essential for a high-performance  $VO_x$ . Specifically, the active oxygen species in  $VO_x$  with a higher oxidation number of +5 is consumed by activating propane molecule to produce propene and water, accompanying the formation of  $VO_r$  with a lower oxidation state (+4 and/or +3), which is re-oxidized to be  $V^{5+}$  by CO<sub>2</sub> for the simultaneous formation of CO. If the weak oxidizing ability of CO<sub>2</sub> is taken into account, the re-oxidation of V<sup>4+</sup> and/or  $V^{3+}$  to  $V^{5+}$  by  $CO_2$  may be a key step in the redox cycle. With these considerations, the catalytic performance of different VO<sub>x</sub> species for CO<sub>2</sub>-ODP may be closely related to their different abilities for activating and converting CO<sub>2</sub> molecules. However, the detailed mechanistic understandings are still of lacking, and only the partial re-oxidation of the reduced  $VO_x$ species by CO<sub>2</sub> is reported.<sup>20,21</sup>

As a common practice, supported VO<sub>x</sub> with the structures of monomeric VO<sub>x</sub>, less or highly polymeric VO<sub>x</sub> and even crystalline V<sub>2</sub>O<sub>5</sub> can be achieved by adjusting the V loadings of the catalyst. However, in this case, the V loadings commonly vary in large ranges from about 0.3 wt% to 20 wt%,<sup>22–24</sup> which makes it difficult to unambiguously correlate the catalytic performance of VO<sub>x</sub> catalysts with their structures. This can be reflected from different observations for oxidative dehydrogenation of propane with  $O_2$  catalyzed by  $VO_r/Al_2O_3$ , *i.e.*, the decreased<sup>25</sup> and constant<sup>26</sup> TOF of propane with increasing the V loadings. On the one hand, the catalyst with a very low V loading makes it difficult to perform the accurately qualitative and quantitative analysis of the characterization and reaction results, thus a lager error may be present. On the other hand, if the loading of V is too high, the intrinsic concentration of the adsorption and activation of feed components and reaction products on per active site of V on the catalyst surface during the reaction, may be affected by the steric constraint effect, leading to an inauthentic conclusion when the reaction results are discussed. Thus, the catalysts with different VO<sub>x</sub> structures while narrow V loading distributions are desired for better understanding the essential reason of the VO<sub>x</sub> structural effects on the catalytic performance of  $VO_x$  for  $CO_2$ -ODP.

As a matter of fact, in addition to adjusting V loadings, the catalysts with different  $VO_x$  structures can be also obtained by changing the preparation methods.<sup>27,28</sup> To date, the widely reported methods for preparing supported  $VO_x$  catalysts are one-step direct synthesis and impregnation method.<sup>29,30</sup> Generally, at a given loading of V, the  $VO_x$  species prepared by one-step synthesis shows a higher dispersion than that synthesized by the impregnation method due to the incorporation of  $VO_x$  species into the framework of the support.<sup>31</sup> Additionally, supported crystalline  $V_2O_5$  can be obtained by the directly physical grinding method due to the weakened interaction between the  $VO_x$  precursor and the support.<sup>32,33</sup>

Based on these understandings, in this work,  $VO_x/(-)SiO_2$ catalysts with 4-6 wt% V loadings are purposefully designed and prepared by different methods. As a result, well-defined structures of  $VO_x$  species over the catalysts, *i.e.*, monomeric  $VO_x$ , less polymeric  $VO_x$ , highly polymeric  $VO_x$  and crystalline V<sub>2</sub>O<sub>5</sub>, are achieved as confirmed from the characterization results. More importantly, the structural impacts of different  $VO_x$  species on the activations of C-O bonds in  $CO_2$  are rigorously revealed from the results of the pulse experiments, and the balance between the activations of C-O bonds in CO2 and C-H bonds in C<sub>3</sub>H<sub>8</sub> molecules induced from different VO<sub>r</sub> species is established together with the reaction and characterization data. These understandings can provide important contributions to the essential reason of the structural impacts of  $VO_x$  species on  $CO_2$ -ODP, especially the activations of C–O bonds in CO<sub>2</sub> and the balance between the activations of C–O bonds in CO2 and C-H bonds in C3H8 molecules, which are key factors in determining the catalytic activity and stability of the catalysts.

### 2. Experimental

#### 2.1. Catalyst preparation

The one-pot hydrothermal synthesis<sup>29</sup> was used to prepare the  $SiO_2$ -supported  $VO_x$  catalyst with a V loading of 4 or 6 wt%. In

the detailed procedure, 1.74 g of cetyltrimethyl ammonium bromide (CTAB,  $\geq$  99.0%, Guanghua Sci-Tech Co., Ltd, Guangdong, China) and 0.25 g of sodium hydroxide (NaOH,  $\geq$  96.0%, Guanghua Sci-Tech Co. Ltd, Guangdong, China) were dissolved into 70 mL of deionized water. The ammonium metavanadate with desired amount (NH<sub>4</sub>VO<sub>3</sub>,  $\geq$  99.0%, Fuchen Chemical Reagent Co. Ltd, Tianjin, China) was dissolved into 25 mL of deionized water at 60 °C. Then, above solutions were completely mixed at 60 °C under magnetic stirring. After 30 min, 9.14 mL of tetraethyl orthosilicate (TEOS, 98.0%, Macklin Biochemical Co. Ltd, Shanghai, China) was slowly dropped into the mixture under magnetic stirring. After 2 h, the obtained mixture was transferred to a Teflon autoclave and crystallized at 120 °C for 2 days. The solids were centrifuged, washed several times by water and ethanol until the pH value of filtrate is neutral, and then dried at 120 °C for 6 h and calcined in air at 600 °C for 3 h. The obtained catalysts were named as 4VO<sub>x</sub>-SiO<sub>2</sub>-H and 6VO<sub>x</sub>-SiO<sub>2</sub>-H, respectively, where 4 and 6 are the weight percent of V (wt%), and H represents the hydrothermal synthesis method.

The incipient wetness impregnation method was applied to prepare the SiO<sub>2</sub>-supported VO<sub>x</sub> catalyst with a V loading of 6 wt%. Before loading VO<sub>x</sub>, SiO<sub>2</sub> with a BET surface area of 580 m<sup>2</sup> g<sup>-1</sup> and an average pore diameter of 3.0 nm (Fuji Silysia Chemical Ltd, Kasugai Aichi, Japan) was pre-treated in air at 600 °C for 3 h. After impregnating the desired amounts of aqueous solution of NH<sub>4</sub>VO<sub>3</sub> assisted by oxalic acid (99.6%, Sinopharm Chemical Reagent Co. Ltd) at a molar ratio of 1/2, the sample was dried at 120 °C for 6 h and then calcined in air at 600 °C for 3 h. The obtained catalyst was named as  $6VO_x/SiO_2$ -I, where 6 is the V loading (wt%), and I represents the impregnation method.

The SiO<sub>2</sub>-supported VO<sub>x</sub> catalyst with a V loading of 6 wt% was also prepared by the physical grinding method. The same SiO<sub>2</sub> support (2 g) to that used in the impregnation experiment was directly blended with 0.275 g of NH<sub>4</sub>VO<sub>3</sub> powders. After grinding for 30 min in an agate mortar, the sample was dried at 120 °C for 6 h and calcined in air at 600 °C for 3 h, leading to the catalyst of  $6VO_x/SiO_2$ -P, where 6 is the V loading (wt%), and P represents the physical grinding method.

#### 2.2. Catalyst characterizations

The loading of V over the catalyst was determined by inductively coupled plasma mass spectrometry (ICP-MS, Bruker Dalton-Aurora M90). Before the test, about 10.0 mg of sample was dissolved in a mixed solution of HNO<sub>3</sub> (Sinopharm, 70%) and HF (Sinopharm,  $\geq$  30%) at 60 °C for 30 min.

 $N_2$  physical adsorption/desorption isotherms were performed on a Bel-sorp-Max instrument at -196 °C. Before the measurement, each sample was pre-treated at 300 °C under vacuum for 10 h. The Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method were employed to calculate specific surface area and pore size distribution (PSD) of the catalysts, respectively.

Powder X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer equipped with Cu-K $\alpha$  radiation (Bruker D8 Advance, 40 kV, 40 mA). The sample was scanned from  $2\theta$  value of  $10^{\circ}$  to  $80^{\circ}$  with a speed of 0.2 s per step.

Raman spectra of the fresh catalysts in the range of 200– 1200 cm<sup>-1</sup> were obtained by a confocal microprobe laser Raman spectrometer (HORIBA Jobin Yvon) equipped with the laser of 325 and 532 nm, respectively. The peak at 520.7 cm<sup>-1</sup> of a silica standard was used to calibrate the obtained spectra. The sample was loaded into an *in situ* cell (Harrick, HVCDR2) and dehydrated at 400 °C under dried Ar (40 mL min<sup>-1</sup>) for 40 min. After cooling to ambient temperature in an Ar flow, Raman spectra were collected. The Raman spectra of the spent catalysts for CO<sub>2</sub>-ODP were directly recorded in the range of 1100– 1700 cm<sup>-1</sup> with the laser of 532 nm at ambient environment.

In situ UV-Vis diffuse reflectance spectra (UV-Vis DRS) were acquired on a PerkinElmer Lambda 950 spectrophotometer equipped with an *in situ* cell (Harrick, HVCDR2). The sample was previously diluted with BaSO<sub>4</sub> ( $\geq$  99.0%, Macklin Biochemical Co. Ltd, Shanghai, China), and then pre-treated at 400 °C under Ar (30 mL min<sup>-1</sup>) for 40 min. After cooling to room temperature, the spectra were recorded in the range of 200–800 nm by using BaSO<sub>4</sub> as the background. The absorption edge energy ( $E_g$ ) was determined by the intercept of the straight line, which is fitted through the low energy rise in  $[F(R_{\infty}) \cdot h\nu]^2$  versus the photon energy plot ( $h\nu$ ), where  $F(R_{\infty})$  is the Kubelka–Munk function.

Temperature-programmed reduction with H<sub>2</sub> (H<sub>2</sub>-TPR) tests were carried out using an Autochem 2920 instrument (Micromeritics, USA) equipped with a thermal conductivity detector (TCD). 100.0 mg of sample was pre-treated at 400 °C for 30 min in an Ar flow (30 mL min<sup>-1</sup>). After cooling to 50 °C, the sample was heated from 50 to 800 °C with a rate of 10 °C min<sup>-1</sup> in a 10 vol% H<sub>2</sub>/Ar flow (30 mL min<sup>-1</sup>). H<sub>2</sub> consumption was monitored and determined by a pre-calibrated TCD.

X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra spectrometer (KRATOS Analytical Ltd) equipped with an Al-K $\alpha$  radiation source (1486.6 eV). The C 1s spectrum at 284.6 eV was applied to calibrate the obtained spectra of the samples.

CO<sub>2</sub> pulse experiments were performed on an AutoChem 2950 HP Chemisorption instrument (Micromeritics, USA). 0.25 g of catalyst was pre-reduced by 10 vol% H<sub>2</sub>/Ar (30 mL min<sup>-1</sup>) at 600 °C for 1 h. After purging with Ar (30 mL min<sup>-1</sup>) for 30 min, pulse of CO<sub>2</sub> (0.5 mL loop) mixed with a flow of Ar (20 mL min<sup>-1</sup>) passed through the reduced catalyst. The temporal change of CO<sub>2</sub> (m/z = 44) and the product of CO (m/z = 28) were monitored by an HPR QIC20 mass spectrometer (MS, Hiden Analytical, United Kingdom). Because the energy of ion source used in MS is relatively low (electron energy: 18.0 V; emission: 50 µA), the signal of 28 (m/z) from CO<sub>2</sub> is negligible.

Thermo gravimetric and differential scanning calorimetry tests (TG-DSC) for the spent catalysts were carried out on a Q600SDT Thermoanalyzer System (TA Instruments). About 5.0 mg of sample was heated from 30 to 800 °C with a heating ramp of 10 °C min<sup>-1</sup> in a flow of air (50 mL min<sup>-1</sup>).

#### 2.3. Catalytic tests

Reaction tests were performed at 0.1 MPa in a quartz fixed-bed reactor (6 mm, i.d.). For each test, 0.25 g of catalyst (40–60 mesh) was loaded into the reactor. Firstly, the sample was pre-

treated at 600 °C for 30 min in an Ar flow of 20 mL min<sup>-1</sup>, and then the gas mixture of  $Ar/C_3H_8/CO_2$  (32 mL min<sup>-1</sup>) in a molar ratio of 2/3/27 passed through the catalyst, where Ar is an internal standard gas. The products and unconvertible  $C_3H_8$ and  $CO_2$  were analyzed by an online gas chromatograph (GC7920, Peking CEAULIGHT) equipped with TCD (TDX-01 column) and flame ionization detector (FID, Porapak Q column). Conversion of propane and  $CO_2$ , and selectivity of different hydrocarbon products (CH<sub>4</sub>,  $C_2H_4$ ,  $C_2H_6$  and  $C_3H_6$ ) were calculated by eqn (1)–(3), respectively.

Carbon balances for all catalysts during the reaction calculated by eqn (4) were centered at 99.3  $\pm$  0.7% (Fig. S1, ESI<sup>†</sup>), indicating a very small amount of coke deposits formed on the catalyst surface. Thus, by assuming that the carbon balance is 100%, the selectivity of CO produced from C<sub>3</sub>H<sub>8</sub> via the reforming of propane with CO<sub>2</sub> reaction (CO<sub>2</sub>-RP) was estimated by subtracting the sum of the hydrocarbon products (CH<sub>4</sub> + C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>6</sub>) from 100% (eqn (5)) according to ref. 13 and 34.

$$C_{3}H_{8} \text{ conversion} = \frac{[F_{C_{3}H_{8}}]_{\text{inlet}} - [F_{C_{3}H_{8}}]_{\text{outlet}}}{[F_{C_{3}H_{8}}]_{\text{inlet}}} \times 100\%$$
(1)

$$CO_2 \text{ conversion} = \frac{[F_{CO_2}]_{\text{inlet}} - [F_{CO_2}]_{\text{outlet}}}{[F_{CO_2}]_{\text{inlet}}} \times 100\%$$
(2)

Selectivity of product 
$$i = \frac{n_i \times [F_i]_{\text{outlet}}}{3 \times \left( [F_{C_3H_8}]_{\text{inlet}} - [F_{C_3H_8}]_{\text{outlet}} \right)} \times 100\%$$
 (3)

Carbon balance

$$=\frac{\sum_{i} n_{i} \times [F_{i}]_{\text{outlet}} + 3 \times [F_{C_{3}H_{8}}]_{\text{outlet}} + [F_{CO}]_{\text{outlet}} + [F_{CO_{2}}]_{\text{outlet}}}{3 \times [F_{C_{3}H_{8}}]_{\text{inlet}} + [F_{CO_{2}}]_{\text{inlet}}}$$

(4)

 $\times$  100%

$$CO \text{ selectivity} = \left(1 - \sum_{i} \frac{n_i \times [F_i]_{\text{outlet}}}{3 \times \left(\left[F_{C_3H_8}\right]_{\text{inlet}} - \left[F_{C_3H_8}\right]_{\text{outlet}}\right)}\right) \times 100\%$$
(5)

where,  $F_{C_3H_8}$ ,  $F_{CO_2}$  and  $F_{CO}$  is the volumetric flow rate (mL min<sup>-1</sup>) of C<sub>3</sub>H<sub>8</sub>, CO<sub>2</sub> and CO, respectively, *i* stands for the detected hydrocarbon product of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> or C<sub>3</sub>H<sub>6</sub>, and  $F_i$  and  $n_i$  represent the flow rate and carbon number of the hydrocarbon product, respectively.

Relative deactivation rate (R) calculated by eqn (6) was used to evaluate the stability of catalyst.

$$R = \frac{X_{\text{initial}} - X_{\text{final}}}{X_{\text{initial}}} \times 100\%$$
(6)

where  $X_{\text{initial}}$  and  $X_{\text{final}}$  is the initial and final conversion of propane or CO<sub>2</sub> at time on stream (TOS) of 8 and 128 min, respectively. High *R* value means low stability of the catalyst.

To estimate the effects of the internal or external diffusion limitations on the catalytic performance, the Weisz-Prater  $(C_{WP})$  and Mears' criteria  $(C_{MM})$  were used for  $6VO_x$ -SiO<sub>2</sub>-H with the highest propane conversion according to ref. 35–37. The detailed calculations are given in Section 12 in the ESI.<sup>†</sup> The calculated  $C_{WP}$  of  $1.54 \times 10^{-3}$  and  $C_{MM}$  of  $2.82 \times 10^{-3}$  are significantly lower than those of the critical values of 1 and 0.15, respectively. This suggests that both internal and external diffusion limitations are negligible for the applied reaction conditions.

The propane consumption rate  $(r(C_3H_8), \text{ mmol } \text{g}^{-1} \text{ min}^{-1})$  was calculated using eqn (7). The apparent  $\text{TOF}(C_3H_8)$  defined as the number of  $C_3H_8$  molecules converted per V atom per hour over the catalysts was calculated by eqn (8), and the  $\text{TOF}(\text{CO}_2)$  was determined through the same method. The data were determined after a TOS of 5 min at a low propane/CO<sub>2</sub> conversion below 10% by adjusting the amount of the loaded catalyst under the conditions of 600 °C, 0.1 MPa,  $\text{Ar}/\text{C}_3\text{H}_8/\text{CO}_2/$ He molar ratio = 2/3/3/24, total flow rate = 32 mL min<sup>-1</sup>.

$$r(C_{3}H_{8}) = \frac{[F_{C_{3}H_{8}}]_{inlet} - [F_{C_{3}H_{8}}]_{outlet}}{22\,400 \times m_{cat}}$$
(7)

$$TOF(C_3H_8) = \frac{r(C_3H_8) \times 60}{c}$$
 (8)

where 22 400,  $m_{\text{cat}}$  and *c* stand for the molar volume at standard conditions (mL mol<sup>-1</sup>), catalyst mass (g), and the content of V over the catalyst (mmol g<sup>-1</sup>), respectively.

### 3. Results and discussion

#### 3.1. Structural and chemical properties of the catalysts

The amounts of V over the  $4VO_x$ -SiO<sub>2</sub>-H,  $6VO_x$ -SiO<sub>2</sub>-H,  $6VO_x$ /SiO<sub>2</sub>-I and  $6VO_x$ /SiO<sub>2</sub>-P catalysts were determined by ICP-MS. According to the results given in Table 1, the nominal V loading of  $4VO_x$ -SiO<sub>2</sub>-H is exactly the same, to the measured value of 4.0 wt% within the experimental errors. In the cases of the catalysts with 6 wt% V, the measured values (5.7–5.8 wt%) are also very close to the nominal V loadings.

XRD results of the catalysts are shown in Fig. 1a. For  $4VO_x$ -SiO<sub>2</sub>-H and  $6VO_x$ -SiO<sub>2</sub>-H, only a broad peak at about 22.6° corresponding to the SiO<sub>2</sub> support with amorphous nature was detected, suggesting the presence of highly dispersed  $VO_x$  species. Contrary to this, additionally weak reflections at  $2\theta$  of 20.3°, 26.2° and 31.1° were observed for  $6VO_x$ /SiO<sub>2</sub>-I, which are assigned to (001), (110), and (400) crystal planes of crystal-line  $V_2O_5$ , respectively.<sup>18,22</sup> In the case of  $6VO_x$ /SiO<sub>2</sub>-P, the more

 Table 1
 Measured V loading and calculated specific surface area of the catalysts

Catalyst	V loading (wt%)	Surface area $(m^2 g^{-1})$
4VO <sub>x</sub> -SiO <sub>2</sub> -H	4.0	810
6VO <sub>x</sub> -SiO <sub>2</sub> -H	5.7	809
6VO <sub>x</sub> /SiO <sub>2</sub> -I	5.8	518
6VO <sub>x</sub> /SiO <sub>2</sub> -P	5.8	496

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Fig. 1 XRD patterns (a), in situ UV (b) and visible (c) Raman spectra, in situ UV-vis DRS spectra (d), calculated edge energy (e) and H<sub>2</sub>-TPR profiles (f) of the catalysts.

and stronger diffraction peaks assigned to crystalline  $V_2O_5$  were observed. These results indicate that the structures of  $VO_x$  over these catalysts are different, even though the V loadings are in a narrow distribution. The  $4VO_x$ -SiO<sub>2</sub>-H and  $6VO_x$ -SiO<sub>2</sub>-H catalysts prepared by one-pot hydrothermal synthesis show a higher dispersion of  $VO_x$ .

Textural properties of the catalysts were analyzed by N<sub>2</sub> adsorption–desorption isotherms. As given in Fig. S2a (ESI<sup>†</sup>), all catalysts exhibited the similar type-IV isotherms with an H1-type hysteresis loop, which are typical characteristics of the capillary condensation of N<sub>2</sub> in mesoporous materials with uniform channels. This can be further reflected from the very narrow PSD peaks at about 3 nm determined by the BJH method (Fig. S2b, ESI<sup>†</sup>). From the calculated textural parameters summarized in Table 1, the specific surface areas of  $4VO_x$ -SiO<sub>2</sub>-H and  $6VO_x$ -SiO<sub>2</sub>-H were about ~ 800 m<sup>2</sup> g<sup>-1</sup>, which are clearly higher than that of  $6VO_x/SiO_2$ -I and  $6VO_x/SiO_2$ -P (~ 500 m<sup>2</sup> g<sup>-1</sup>). This commonly leads to a higher dispersion of VO<sub>x</sub>, coinciding with the XRD results (Fig. 1a).

To further identify the structure of  $VO_x$  species over these catalysts, *in situ* UV and visible Raman were applied under

dehydrated conditions. Generally, the former is more sensitive to detect isolated and polymerized VO<sub>x</sub> species, while the latter shows a higher sensitivity to crystalline V<sub>2</sub>O<sub>5</sub>.<sup>22,23,38</sup> As shown in the Fig. 1b, two UV Raman bands at  $\sim 460$  and 1030 cm<sup>-1</sup> were clearly observed over 4VOx-SiO2-H and 6VOx-SiO2-H, which can be assigned to V-O-Si and V=O stretching vibrations, respectively.<sup>38-40</sup> However, an additionally weak Raman band at 994 cm<sup>-1</sup> was detected for 6VO<sub>x</sub>/SiO<sub>2</sub>-I and 6VO<sub>x</sub>/SiO<sub>2</sub>-P, indicating the presence of crystalline  $V_2O_5$ .<sup>22,41</sup> This can be more clearly reflected by the visible Raman spectra as given in Fig. 1c. Only the Raman band at  $\sim 1035$  cm<sup>-1</sup> and the weak and broad band at about 484 cm<sup>-1</sup> assigned to V=O vibration and the SiO<sub>2</sub> support,<sup>38,40</sup> respectively, were observed in the spectra of 4VO<sub>x</sub>-SiO<sub>2</sub>-H and 6VO<sub>x</sub>-SiO<sub>2</sub>-H. However, the Raman bands at 273, 398, 472, 514, 686, and 994 cm<sup>-1</sup> assigned to crystalline V<sub>2</sub>O<sub>5</sub> were clearly observed in the case of 6VO<sub>x</sub>/SiO<sub>2</sub>-I.<sup>40</sup> Furthermore, the intensity of these Raman bonds becomes more pronounced in the spectrum of 6VO<sub>x</sub>/SiO<sub>2</sub>-P, accompanying an almost disappearance of V $\equiv$ O vibration at 1035 cm $^{-1}$ . This suggests the formation of dominated crystalline V2O5 over 6VO<sub>x</sub>/SiO<sub>2</sub>-P.

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To estimate the polymerization degree of  $VO_x$  over these catalysts, in situ UV-Vis DRS experiments were performed under dehydrated condition. As shown in Fig. 1d, a broad absorption band from about 200 to 550 nm was observed in all the spectra of the catalysts because of the ligand-to-metal charge transfer (LMCT) transitions and the d-d transitions of V ions. According to ref. 42 and 43 the coordination and polymerization degree of VO<sub>x</sub> species are closely connected with the band position of LMCT transitions. Specifically, the absorption features at 222 and 243 nm can be assigned to strongly and less distorted isolated  $VO_x$  in tetrahedral coordination environment, respectively.<sup>31,44</sup> The bands at 325 and 385 nm are generally assigned to oligomeric VO<sub>r</sub> species in either tetrahedral or octahedral coordination environment.37,45 Additionally, the octahedral V<sub>2</sub>O<sub>5</sub> crystallites can be observed at  $\sim$  510 nm.<sup>37,45</sup> For  $4VO_x$ -SiO<sub>2</sub>-H, the strongest bonds at 222 and 243 nm were observed. However, the intensity of these two bonds was decreased over 6VO<sub>x</sub>-SiO<sub>2</sub>-H, accompanying the enhanced signals at 325 and 385 nm. This indicates that the 4VO<sub>x</sub>-SiO<sub>2</sub>-H catalyst shows the most isolated  $VO_x$  species, while more polymeric  $VO_r$  was formed over  $6VO_r$ -SiO<sub>2</sub>-H. In the case of  $6VO_x/SiO_2$ -I, an extremely weak band at 510 nm was observed, indicating the presence of both polymeric  $VO_x$  and a small amount of crystalline V<sub>2</sub>O<sub>5</sub>. As for 6VO<sub>x</sub>/SiO<sub>2</sub>-P, the intensity of the band at 510 nm became more pronounced, suggesting the presence of higher amount of crystalline V<sub>2</sub>O<sub>5</sub>.

Furthermore, the edge energy  $(E_g)$  of these catalysts was determined based on the UV-Vis DRS results. As shown in Fig. S3 (ESI<sup>†</sup>) and 1e, the calculated  $E_g$  decreased in the order of 4VO<sub>x</sub>-SiO<sub>2</sub>-H (3.48 eV) > 6VO<sub>x</sub>-SiO<sub>2</sub>-H (3.32 eV) > 6VO<sub>x</sub>/ SiO<sub>2</sub>-I (2.90 eV) > 6VO<sub>x</sub>/SiO<sub>2</sub>-P (2.50 eV), indicating an increased degree of polymerization or domain size of VO<sub>x</sub>.<sup>18,24</sup> Moreover, the  $E_g$  for 4VO<sub>x</sub>-SiO<sub>2</sub>-H was very close to that for the bulk Na<sub>3</sub>VO<sub>4</sub> (3.55 eV) only consisting of isolated VO<sub>x</sub> species.<sup>46</sup> Thus, the isolated VO<sub>x</sub> species was dominated over 4VO<sub>x</sub>-SiO<sub>2</sub>-H. However, in the case of 6VO<sub>x</sub>/SiO<sub>2</sub>-P, the  $E_g$ was comparable with that of the bulk V<sub>2</sub>O<sub>5</sub> (2.33 eV),<sup>46</sup> suggesting the presence of dominated crystalline V<sub>2</sub>O<sub>5</sub>.

To study the redox property of the VO<sub>x</sub> species over the catalysts, H<sub>2</sub>-TPR was performed. As shown in Fig. 1f, only a reduction peak at around 530 °C was observed for  $4VO_x$ -SiO<sub>2</sub>-H and  $6VO_x$ -SiO<sub>2</sub>-H, which can be easily assigned to the reduction of highly dispersed VO<sub>x</sub> species.<sup>47,48</sup> For  $6VO_x/SiO_2$ -I, two peaks at 541 and 624 °C were observed. The former originates from the reduction of highly dispersed VO<sub>x</sub> species, while the weak peak at 624 °C can be attributed to the reduction of a small

amount of microcrystalline V<sub>2</sub>O<sub>5</sub>.<sup>49</sup> In the case of 6VO<sub>x</sub>/SiO<sub>2</sub>-P, three peaks at 550, 610 and 701 °C were present. The shoulder peak at 550 °C can be assigned to the reduction of a small amount of highly dispersed VO<sub>x</sub> species, while two sharp peaks at higher temperatures originate from the different stages for the reduction of bulk V<sub>2</sub>O<sub>5</sub> from V<sup>5+</sup> to V<sup>4+</sup>, and then to V<sup>3+,50</sup> Moreover, the continuously increased peak temperatures in the order of 4VO<sub>x</sub>-SiO<sub>2</sub>-H (528 °C) < 6VO<sub>x</sub>-SiO<sub>2</sub>-H (536 °C) < 6VO<sub>x</sub>/SiO<sub>2</sub>-F (550, 610 and 701 °C) indicate an increased difficulty in the reduction of the catalysts with a higher polymerization extent or a larger domain size of VO<sub>x</sub> species.<sup>29,49</sup>

As for the oxidation state of V over the fresh catalysts, a symmetric V  $2p_{3/2}$  peak with a binding energy of 517.6 eV was observed in all XP spectra of the catalysts (Fig. S4, ESI†), suggesting that V<sup>5+</sup> is dominated species on the catalysts surface.<sup>18,22</sup> Taking this fact and the total amounts of H<sub>2</sub> consumption during H<sub>2</sub>-TPR into account, the average oxidation state (AOS) of V over different catalysts after H<sub>2</sub>-TPR was calculated. As given in Table 2, the AOS of V decreased in the order of  $4VO_x$ -SiO<sub>2</sub>-H (+4.06) <  $6VO_x$ -SiO<sub>2</sub>-H (+3.88) <  $6VO_x$ /SiO<sub>2</sub>-I (+3.62) <  $6VO_x$ /SiO<sub>2</sub>-P (+3.35). This indicates that the reduction degree of VO<sub>x</sub> species increases with increasing its polymerization degree or domain size, leading to a more favorable reduction of V<sup>5+</sup> to V<sup>3+</sup> instead of V<sup>4+.18,22</sup>

Based on these complementary characterizations, the dominated structures of VO<sub>x</sub> over the four catalysts are proposed and illustrated in Scheme 1. It can be concluded that (1) monomeric VO<sub>x</sub> species is dominantly present over  $4VO_x$ -SiO<sub>2</sub>-H; (2) monomeric and less polymeric VO<sub>x</sub> coexist over the  $6VO_x$ -SiO<sub>2</sub>-H catalyst; (3) highly polymeric VO<sub>x</sub> and a small amount of crystalline V<sub>2</sub>O<sub>5</sub> are present over  $6VO_x/SiO_2$ -I; and (4) crystalline V<sub>2</sub>O<sub>5</sub> is overwhelmingly dominated in the case of  $6VO_x/SiO_2$ -P.

#### 3.2. Catalytic performance

The initial conversion of propane and  $CO_2$  at a TOS of 8 min over the catalysts for  $CO_2$ -ODP is given in Fig. 2a. The propane conversion decreased from 41.0% to 11.9% in the order of  $6VO_x$ -SiO<sub>2</sub>-H >  $4VO_x$ -SiO<sub>2</sub>-H >  $6VO_x$ /SiO<sub>2</sub>-I >  $6VO_x$ /SiO<sub>2</sub>-P. If the CO<sub>2</sub> conversion is compared, the same changing order can be observed. Considering the fact that the V loadings of these catalysts are very close, the results suggest that the structure of  $VO_x$  plays an important role in determining the catalytic activity.

As show in Fig. 2b, the initial propene selectivity decreased from 87.3% to 67.7% in the order of  $4VO_x$ -SiO<sub>2</sub>-H >  $6VO_x$ -

Table 2         Calculated results based on the H <sub>2</sub> -TPR and CO <sub>2</sub> pulse experiments of the catalysts										
Catalyst		$H_2 \text{ consumption}^a (\mu \text{mol } g_{\text{catalyst}}^{-1})$	H/V ratio <sup>a</sup>	AOS of $V^a$	Released $CO^{b}$ (µmol $g_{catalyst}^{-1}$ )	Released $CO^{b}$ (mmol $g_{V}^{-1}$ )				
4VO <sub>x</sub> -Si	O <sub>2</sub> -H	358	0.94	+4.06	270	6.74				
6VO <sub>x</sub> -Si	$O_2$ -H	621	1.12	+3.88	353	5.89				
6VO <sub>r</sub> /SiC	$D_2$ -I	766	1.38	+3.62	225	3.76				
6VO <sub>x</sub> /SiC	$\overline{D_2}$ -P	915	1.65	+3.35	36	0.61				

<sup>*a*</sup> Calculated based on the H<sub>2</sub>-TPR results as given in Fig. 1f. <sup>*b*</sup> Cumulative amount of CO formed from the pulse of CO<sub>2</sub> over the reduced catalyst at 600  $^{\circ}$ C as given in Fig. 4a–d.



Scheme 1 Illustration of the dominated VO<sub>x</sub> species over 4VO<sub>x</sub>-SiO<sub>2</sub>-H (a), 6VO<sub>x</sub>-SiO<sub>2</sub>-H (b), 6VO<sub>x</sub>/SiO<sub>2</sub>-I (c) and 6VO<sub>x</sub>/SiO<sub>2</sub>-P (d).



Fig. 2 Initial conversion of  $C_3H_8$  and  $CO_2$  (a),  $C_3H_6$  selectivity (b) and by-products selectivity (c), and the relative deactivation rate (d) over the catalysts for  $CO_2$ -ODP under the conditions of 600 °C, 0.1 MPa,  $Ar/C_3H_8/CO_2$  molar ratio = 3/2/27, total flow rate = 32 mL min<sup>-1</sup>, and GHSV = 7680 mL g<sup>-1</sup> h<sup>-1</sup>.

SiO<sub>2</sub>-H > 6VO<sub>x</sub>/SiO<sub>2</sub>-I » 6VO<sub>x</sub>/SiO<sub>2</sub>-P. To understand the main side reactions, the initial selectivity of gaseous by-products was analyzed. As shown in Fig. 2c, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> originating from the cracking and CO produced from the CO<sub>2</sub>-RP reaction were detected. For all catalysts, the total selectivity for the byproducts of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> was centered at around 5%. However, the selectivity of CO increased from 7.6% to 26.0% in the order of 4VO<sub>x</sub>-SiO<sub>2</sub>-H < 6VO<sub>x</sub>-SiO<sub>2</sub>-H < 6VO<sub>x</sub>/SiO<sub>2</sub>-I « 6VO<sub>x</sub>/SiO<sub>2</sub>-P. The change order is inverse to that of the propene selectivity (Fig. 2b), suggesting that the formation of desired propene is strongly affected by the side reaction of  $CO_2$ -RP during the reaction. The  $4VO_x$ -SiO<sub>2</sub>-H catalyst with the highest dispersion of  $VO_x$  species, *i.e.*, the dominantly monomeric  $VO_x$ , showed the highest propene selectivity. With increasing the degree of polymerization or domain size of  $VO_x$ , the amounts of active site over the catalyst which are favorable for  $CO_2$ -RP involving the breaking of C–C bond increased, leading to the lowest propene selectivity over the  $6VO_x/SiO_2$ -P catalyst with dominantly crystalline V<sub>2</sub>O<sub>5</sub>. A similar result is observed in the chemical looping oxidative dehydrogenation of propane catalyzed by VO<sub>x</sub>/TiO<sub>2</sub>, suggesting that the highly dispersed VO<sub>x</sub> is the main active species for the oxidative dehydrogenation of propane.<sup>51</sup>

In the case of the catalytic stability, an apparently decreased conversion of either propane or CO<sub>2</sub> with increasing TOS was observed for all catalysts (Fig. S5a and b, ESI<sup>†</sup>). To quantitatively estimate the stability of the catalysts, the relative deactivation rate associated with propane conversion was calculated ( $R_{\text{propane}}$ , see eqn (6)). As given in Fig. 2d, the stability of the catalysts varied in a lager extent, and  $R_{\text{propane}}$  increased in the order of  $4\text{VO}_x$ -SiO<sub>2</sub>-H <  $6\text{VO}_x$ -SiO<sub>2</sub>-H <  $6\text{VO}_x$ /SiO<sub>2</sub>-I <  $6\text{VO}_x$ /SiO<sub>2</sub>-I <  $6\text{VO}_x$ /SiO<sub>2</sub>-F. The same change pattern was observed when the relative deactivation rate was calculated based on the CO<sub>2</sub> conversion ( $R_{\text{CO}_2}$ , Fig. S6, ESI<sup>†</sup>), resulting in the best stability of the 4VO<sub>x</sub>-SiO<sub>2</sub>-H catalyst.

#### 3.3. Structural correlation of $VO_x$ with the catalytic activity

As revealed from the results in Sections 3.1 and 3.2, the catalytic activity of supported  $VO_x$  for  $CO_2$ -ODP is closely connected with the polymerization extent or domain size of  $VO_x$  species. To further confirm this, the apparent  $TOF(C_3H_8)$  of the catalysts calculated by eqn (8) were correlated with the  $E_{g}$  values derived from the UV-vis DRS. As shown in Fig. 3, with decreasing the  $E_{\alpha}$ , the TOF( $C_3H_8$ ) continuously decreased in the order of  $4VO_x$ - $SiO_2-H > 6VO_r-SiO_2-H > 6VO_r/SiO_2-I > 6VO_r/SiO_2-P$ , leading to the highest  $TOF(C_3H_8)$  of  $4VO_x$ -SiO<sub>2</sub>-H with dominantly monomeric VO<sub>x</sub>. In the case of the 4VO<sub>x</sub>-SiO<sub>2</sub>-H and 6VO<sub>x</sub>-SiO<sub>2</sub>-H catalysts, no crystalline V<sub>2</sub>O<sub>5</sub> can be detected, and only two-dimensional  $VO_x$  species is present. Moreover, the textural properties of 4VO<sub>x</sub>-SiO<sub>2</sub>-H and 6VO<sub>x</sub>-SiO<sub>2</sub>-H, *i.e.* the surface area and pore size distributions are almost the same (Table 1 and Fig. S2, ESI<sup>†</sup>), which commonly leads to the very similar V distributions on the SiO<sub>2</sub> support. Thus, the decreased  $TOF(C_3H_8)$  can be ascribed to the increased in the polymerization degree of  $VO_x$ .<sup>16,17</sup> However, the crystalline  $V_2O_5$  is formed



Fig. 3 Relationship between TOF(C<sub>3</sub>H<sub>8</sub>) and  $E_{g}$  derived from UV-vis DRS of the catalysts.

over the 6VO<sub>x</sub>/SiO<sub>2</sub>-I and 6VO<sub>x</sub>/SiO<sub>2</sub>-P catalysts, in which not all V atoms can be touched with the reactants during the reaction. Thus, the decreased TOF(C<sub>3</sub>H<sub>8</sub>) from 6VO<sub>x</sub>/SiO<sub>2</sub>-I to 6VO<sub>x</sub>/SiO<sub>2</sub>-P is determined by both the increased polymerization degree of  $VO_x$  and the formation of more crystalline  $V_2O_5$ . These analyses together with the structures of VO<sub>r</sub> illustrated in Scheme 1 indicate that the activity of VO<sub>x</sub> species for CO<sub>2</sub>-ODP decreases in the order of monomeric  $VO_r > less polymeric VO_r > highly$ polymeric  $VO_x > crystalline V_2O_5$ . If the apparent  $TOF(CO_2)$  of the catalyst was calculated and correlated with the  $E_{\alpha}$  (Fig. S7, ESI<sup>†</sup>), exactly the same change pattern to that of the  $TOF(C_3H_8)$ was observed, and the highest value was obtained over 4VO<sub>x</sub>-SiO<sub>2</sub>-H, indicating the simultaneous activation of propane and  $CO_2$ . Moreover, the TOF( $CO_2$ ) of the catalyst is generally lower than its  $TOF(C_3H_8)$ , which can be attributed to the weak ability for the activation of  $CO_2$  over the supported  $VO_x$  species.<sup>52</sup>

According to the Mars-van Krevelen redox mechanism for CO<sub>2</sub>-ODP catalyzed by supported VO<sub>x</sub> catalysts,<sup>8,53</sup> the activated propane molecules abstract the active oxygen from the VO<sub>r</sub> species with a high V oxidation state (+5) to produce propene and water. Simultaneously, VO<sub>x</sub> at a reduced state is re-oxidized by the activated  $CO_2$  to complete the redox cycle of  $VO_x$  with releasing CO. Thus, the re-oxidized ability of  $V^{3+}/V^{4+}$  by CO<sub>2</sub> may be crucial in determining the activity of the catalyst, if the facile redox property of supported  $VO_x$  at high temperatures and the soft oxidizing ability of CO<sub>2</sub> are taken into account. Following this understanding, the re-oxidized ability of the reduced catalysts by CO2 was investigated by CO2 pulse experiments at the reaction temperature of 600 °C. As shown in Fig. 4a–d, when CO<sub>2</sub> (m/z = 44) was pulsed, CO (m/z = 28) was detected over all the catalysts pre-reduced by H<sub>2</sub>. Moreover, for pure SiO<sub>2</sub> support prepared by hydrothermal synthesis method, no CO signal (m/z = 28) was detected (Fig. S8, ESI<sup>+</sup>). These results indicate that the reduced VO<sub>x</sub> species can be re-oxidized by  $CO_2$  to replenish the oxygen species consumed by  $H_2$ reduction. Moreover, as shown in Table 2, the amounts of released CO per gram of the catalyst varied in a large range, and decreased from 353 to 36  $\mu$ mol  $g_{catalyst}^{-1}$  in the order of  $6VO_x$ -SiO<sub>2</sub>-H >  $4VO_x$ -SiO<sub>2</sub>-H >  $6VO_x$ /SiO<sub>2</sub>-I >  $6VO_x$ /SiO<sub>2</sub>-P. This indicates that the re-oxidized ability of reduced  $VO_x$ species by  $CO_2$  is affected by the structure of  $VO_r$  over the parent catalysts. To further confirm this, the amounts of released CO per gram of V over the catalyst were calculated (Table 2), and continuously decreased from 6.74 to 0.61 mmol  $g_v^{-1}$ in the order of  $4VO_x$ -SiO<sub>2</sub>-H >  $6VO_x$ -SiO<sub>2</sub>-H >  $6VO_x$ /SiO<sub>2</sub>-I > 6VO<sub>x</sub>/SiO<sub>2</sub>-P. Thus, the re-oxidized ability of the reduced catalysts by CO<sub>2</sub> decreases with increasing the polymerization extent or domain size of  $VO_x$  over the parent catalysts, and  $4VO_x$ -SiO<sub>2</sub>-H with dominantly monomeric VO<sub>x</sub> shows the best ability for the activation of  $CO_2$  to release CO. As for the reason, on the one hand, the H2-TPR results have demonstrated that the V<sup>5+</sup> oxide species with a higher polymerization extent or domain size over the parent catalysts was more easily reduced to a lower V oxidation state of  $V^{3+}$  rather than  $V^{4+}$  (Table 2), which is difficult to be re-oxidized by  $CO_2$  to  $V^{5+}$  if the soft oxidizing property of CO2 was taken into account.54,55 On the



**Fig. 4** Transient MS response of the consecutive CO<sub>2</sub> pulses over the pre-reduced catalysts at 600 °C (a)–(d), and correlating the propane consumption rate with the amount of cumulatively released CO per gram of catalyst (e) and the TOF( $C_3H_8$ ) with the amount of cumulatively released CO per gram of V (f) during the CO<sub>2</sub> pulse experiments.

other hand, the CO<sub>2</sub> pulse experiments were performed at 600 °C, however the 6VO<sub>x</sub>-SiO<sub>2</sub>-P catalyst, which exhibits a reduction peak at a higher temperature of about 700 °C during H<sub>2</sub>-TPR, may not be fully reduced at 600 °C. This also led to a lower amount of released CO when CO<sub>2</sub> was pulsed. Moreover, the amount of released CO (270 µmol g<sub>catalyst</sub><sup>-1</sup>) during the CO<sub>2</sub> pulse experiments over 4VO<sub>x</sub>-SiO<sub>2</sub>-H with the best ability for the activation of CO<sub>2</sub> is still lower than the amount of H<sub>2</sub> consumption (358 µmol g<sub>catalyst</sub><sup>-1</sup>) during the H<sub>2</sub>-TPR (Table 2). This indicates that the reduced VO<sub>x</sub> species cannot be fully reoxidized by CO<sub>2</sub> owning to the weak oxidizing ability of CO<sub>2</sub>.

Based on these understandings, the consumption rate of propane ( $r(C_3H_8)$ , mmol  $g^{-1}$  min<sup>-1</sup>) was rationally correlated

with the amount of formed CO per gram of catalyst (mmol  $g_{catalyst}^{-1}$ ) determined by CO<sub>2</sub> pulse experiments. As shown in Fig. 4e, a directly proportional relationship was obtained, and  $r(C_3H_8)$  monotonously increased in the order of  $6VO_x/SiO_2$ -P <  $6VO_x/SiO_2$ -I <  $4VO_x$ -SiO<sub>2</sub>-H <  $6VO_x$ -SiO<sub>2</sub>-H with increasing the amount of formed CO. The higher amount of formed CO during the CO<sub>2</sub> pulse experiments means the supplement of more active oxygen species over the reduced catalysts by CO<sub>2</sub> reduction. Thus, this result clearly indicates that the activity of the parent catalyst is determined by the ability in activating CO<sub>2</sub> to replenish the consumed oxygen species of the reduced catalyst, coinciding with the Marsvan-Krevelen redox mechanism. To further understand the

relationship between the structure of VO<sub>x</sub> and the catalytic activity, the TOF(C<sub>3</sub>H<sub>8</sub>) was correlated with the amount of formed CO per gram of V. As shown in Fig. 4f, with increasing the amount of released CO per gram of V, the TOF(C<sub>3</sub>H<sub>8</sub>) increased in the order of  $6VO_x/SiO_2$ -P  $< 6VO_x/SiO_2$ -I  $< 6VO_x$ -SiO<sub>2</sub>-H  $< 4VO_x$ -SiO<sub>2</sub>-H. The reduced  $4VO_x$ -SiO<sub>2</sub>-H catalyst with dominantly monomeric VO<sub>x</sub> species is the most easily reoxidized by CO<sub>2</sub>, thereby the parent catalyst can well complete the redox cycle of VO<sub>x</sub> during CO<sub>2</sub>-ODP, resulting in the highest TOF(C<sub>3</sub>H<sub>8</sub>).

#### 3.4. Insight into the catalytic stability

Generally, the coke deposition on the catalyst surface during the CO<sub>2</sub>-ODP reaction is associated with the catalyst deactivation. Thus, the spent catalysts after a TOS of 128 min were analyzed by TG, and the results are given in Fig. S9a-d (ESI<sup>†</sup>). According to ref. 11 and 16, the weight loss in the temperature range of 25-200 °C is attributed to the removing of adsorbed water, while the weight loss in the temperature range of 200-450 °C can be reasonably assigned to the burning of the deposited coke on catalyst surface. In our case, the coke content of the catalysts determined by the weight loss at 200-450 °C during TG was very low and varied in the range of 0.41 to 0.91% (Table 3). When the coke species was considered, visible Raman was performed for the spent catalysts at ambient environment. As shown in Fig. S10 (ESI $\dagger$ ), typical Raman shifts at 1340 and 1600 cm<sup>-1</sup>, assigning to the disordered (D band) and graphitic carbon (G band),<sup>16,56</sup> respectively, were clearly detected for all the spent catalysts. Generally, the graphitization degree of deposited coke can be estimated by the calculated intensity ratio of the D band to G band  $(I_{\rm D}/I_{\rm G})$ .<sup>16,56</sup> As given in Table 3, the  $I_{\rm D}/I_{\rm G}$  was determined as  $0.74 \pm 0.08$  for  $4VO_x$ -SiO<sub>2</sub>-H,  $6VO_x$ -SiO<sub>2</sub>-H and  $6VO_x$ /SiO<sub>2</sub>-I, indicating the similar coke species on the surface of catalysts. Contrary to this, a clearly lower  $I_D/I_G$  of 0.38 was obtained for 6VO<sub>x</sub>/SiO<sub>2</sub>-P, indicating the highest graphitization extent of coke species.<sup>7,16,56</sup> As revealed from the analyses of the by-product selectivity, the 6VO<sub>x</sub>/SiO<sub>2</sub>-P catalyst with dominated V<sub>2</sub>O<sub>5</sub> is the most favorable to break C-C bond via the CO2-RP and cracking reactions, while the remaining catalysts are more promising for CO<sub>2</sub>-ODP. Thus, the highest graphitization extent of coke species over 6VO<sub>x</sub>/SiO<sub>2</sub>-P may originate from the side reactions, which is favorable to form the coke species with a higher graphitization extent. This is consistent with previous work.<sup>57</sup> Additionally, the coke content decreased in the order of  $6VO_r$ -SiO<sub>2</sub>-H >  $4VO_r$ - $SiO_2-H > 6VO_x/SiO_2-I > 6VO_x/SiO_2-P$ , which coincides well with their propane conversion (Fig. 2a), meaning that the catalyst which converts more propane shows a higher content of coke. Following this understanding, the apparent coking rate, which is defined as the amount of the coke by converting 1 mol propane (g mol<sup>-1</sup>) over the catalyst for CO<sub>2</sub>-ODP was calculated. As given in Table 3, the coking rate was determined as 0.45  $\pm$ 0.03 g mol<sup>-1</sup> for  $4VO_x$ -SiO<sub>2</sub>-H,  $6VO_x$ -SiO<sub>2</sub>-H and  $6VO_x$ /SiO<sub>2</sub>-I, indicating a similar coke deposition behavior on the surface of catalysts. On the contrary, the significantly higher coking rate of 1.05 g mol<sup>-1</sup> was obtained for  $6VO_r/SiO_2$ -P, which coincides well with the highest graphitization extent of coke species

Table 3 Coke deposition analysis and V oxidation state distribution over the spent catalysts for CO<sub>2</sub>-ODP after a TOS of 128 min

	Colta content <sup>a</sup> Colting rat		Colving rate <sup>c</sup>	V oxidation state distribution <sup>d</sup> (%)		
Catalyst	(wt%)	$I_{\rm D}/{I_{\rm G}}^b$	$(g \text{ mol}^{-1})$	V <sup>5+</sup>	$V^{4^+}$	$V^{3^+}$
4VO <sub>x</sub> -SiO <sub>2</sub> -H	0.87	0.82	0.49	69.4	30.6	0
6VO <sub>x</sub> -SiO <sub>2</sub> -H	0.91	0.74	0.50	61.8	31.1	7.1
6VO <sub>x</sub> /SiO <sub>2</sub> -I	0.58	0.66	0.47	51.5	27.0	21.5
6VO <sub>x</sub> /SiO <sub>2</sub> -P	0.41	0.38	1.06	25.1	29.1	45.8

<sup>*a*</sup> Determined by the TG results as given in Fig. S9 (ESI). <sup>*b*</sup> Calculated based on the visible Raman results as given in Fig. S10 (ESI). <sup>*c*</sup> Calculated based on the amount of the coke by converting 1 mol propane. <sup>*d*</sup> Determined by the XP spectra results as given in Fig. 5b.

(Table 3). It is worth noting that if the relative deactivation rate of the catalysts ( $R_{\text{propane}}$ , Fig. 2d) was compared with either the coke content or the coking rate (Table 3), no obvious correlation of the catalytic stability with the deposited coke can be found, suggesting that the coke deposition may be not the critical factor in determining the stability of the catalysts.

According to the redox mechanism of CO<sub>2</sub>-ODP, the ability to replenish the active oxygen species by  $CO_2$  to complete the redox cycles of  $VO_x$  plays an important role in determining the stability of the catalysts. To confirm this viewpoint, the relative deactivation rate  $(R_{propane})$  was correlated with the amount of released CO per gram of V over the catalyst. As shown in Fig. 5a, an almost linear relationship was obtained, *i.e.*, a higher amount of released CO, a lower  $R_{\text{propane}}$ . This indicates that the catalyst shows a better stability provided that the reduced  $VO_x$  species over the catalyst is more easily re-oxidized by CO2. As a result, the best stability was obtained over the 4VOx-SiO2-H catalyst with dominantly monomeric  $VO_x$  species. Taking the structural and chemical properties of different VO<sub>x</sub> species into account, the V<sup>5+</sup> species with a higher polymerization extent or domain size over the parent catalysts was more easily reduced to  $V^{3+}$  (Table 2), which cannot be effectively re-oxidized by CO<sub>2</sub> to V<sup>5+</sup> to complete the redox cycles.<sup>18,54</sup> Thus, the deep reduction of V<sup>5+</sup> to V<sup>3+</sup> during the reaction may be associated with the catalyst deactivation. To confirm this, the spent catalysts after CO<sub>2</sub>-ODP for a TOS of 128 min were characterized by XPS. As shown in Fig. 5b, the binding energy of V 2p3/2 over the spent catalysts shifted to a lower value in comparison with that of the fresh catalysts (517.6 eV, Fig. S4, ESI<sup> $\dagger$ </sup>), indicating an increased content of VO<sub>x</sub> with a lower oxidation state<sup>18,22</sup> after the CO<sub>2</sub>-ODP reaction. To make a quantitative comparison, the V 2p<sub>3/2</sub> spectra were deconvoluted. As given in Fig. 5b, three peaks at 515.7, 516.6 and 517.6 eV assigned to V<sup>3+</sup>, V<sup>4+</sup> and V<sup>5+</sup> species,<sup>22,58</sup> respectively, were observed. The relative fractions of  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$  over the spent catalysts were calculated by respective peak area. As shown in Table 3, the relative fraction of V5+ deceased from 69.4% to 25.1% in the order of  $4VO_x$ -SiO<sub>2</sub>-H >  $6VO_x$ -SiO<sub>2</sub>-H >  $6VO_x$ /SiO<sub>2</sub>-I >  $6VO_x$ /SiO<sub>2</sub>-P, the change pattern is consistent with that of their catalytic stability, *i.e.*, the higher content of V<sup>5+</sup> remained on the spent catalyst surface, the better stability of the catalyst was (Fig. S11a, ESI<sup>+</sup>). Contrary to this, when the relative fraction of V<sup>3+</sup> was correlated with the stability of the catalysts, an opposite order



Fig. 5 Correlation of relative deactivation rate ( $R_{propane}$ ) with the amount of formed CO per gram of V over the catalyst during CO<sub>2</sub> pulse experiments (a), and V  $2p_{3/2}$  XP spectra of the spent catalysts after CO<sub>2</sub>-ODP for a TOS of 128 min (b).

was found (Fig. S11b, ESI<sup>†</sup>). These results clearly indicate that the deep reduction of  $V^{5+}$  to  $V^{3+}$  is the key reason for the deactivation of the catalysts in CO<sub>2</sub>-ODP. Thus, the redox rates of the VO<sub>x</sub> species participated with CO<sub>2</sub> and propane are not very well matched, owning to the weak oxidizing ability of CO<sub>2</sub>. This is consistent with the CO<sub>2</sub> pulse experiments and H<sub>2</sub>-TPR results (Table 2).

Following the above discussion, the redox mechanism of  $CO_2$ -ODP catalyzed by the  $SiO_2$ -supported  $VO_x$  catalysts with isolated  $VO_x$  species is illustrated in Scheme 2. Propane reacts with the active oxygen of  $V^{5+}$  to produce propene and water, resulting in the formation of reduced  $VO_x$  with an oxidation state of +4. To complete the redox cycle,  $CO_2$  reacts with the  $V^{4+}$  species to release CO and simultaneously replenish the active oxygen species. With increasing the polymerization extent or domain size of supported  $VO_x$  species, the matching of the redox cycles of  $VO_x$  during the  $CO_2$ -ODP reaction was hindered, due to the formation of deeply reduced  $VO_x$  species with a lower oxidation state of +3, which cannot be efficiently re-oxidized by

 $CO_2$  to  $V^{5+}$ . As a result of the highest dispersion of  $VO_x$  species over  $4VO_x$ -SiO<sub>2</sub>-H, the best performance for  $CO_2$ -ODP was obtained among the evaluated catalysts.

### 4. Conclusions

In summary, four SiO<sub>2</sub>-supported VO<sub>x</sub> catalysts with narrow distributions of V loading while well-defined structures of VO<sub>x</sub> species were synthesized by applying appropriate preparation methods. The dominated monomeric and less polymeric VO<sub>x</sub> were formed over the 4VO<sub>x</sub>–SiO<sub>2</sub>-H and 6VO<sub>x</sub>–SiO<sub>2</sub>-H catalysts, respectively, prepared by one-pot hydrothermal synthesis. In case of the 6VO<sub>x</sub>/SiO<sub>2</sub>-I catalyst prepared by simply impregnation method, the highly polymerized VO<sub>x</sub> with a small amount of V<sub>2</sub>O<sub>5</sub> was present, while V<sub>2</sub>O<sub>5</sub> crystallites were overwhelmingly predominant over the 6VO<sub>x</sub>/SiO<sub>2</sub>-P catalyst prepared by physic grinding method. The catalytic activity and stability for CO<sub>2</sub>-ODP decreased in the order of 4VO<sub>x</sub>–SiO<sub>2</sub>-H > 6VO<sub>x</sub>–SiO<sub>2</sub>-I > 6VO<sub>x</sub>/SiO<sub>2</sub>-P, which can be explained



Scheme 2 Redox mechanism over supported VO<sub>x</sub> catalyst for CO<sub>2</sub>-ODP.

by the ability for re-oxidation of the reduced  $VO_x$  species with different structures by  $CO_2$ . The reduced monomeric  $VO_x$  is the most easily re-oxidized by  $CO_2$ , and thus the reduction/oxidation cycles of  $V^{4+}/V^{5+}$  species during the  $CO_2$ -ODP reaction can be well completed, leading to the best performance. With increasing the polymerization extent or domain size of supported  $VO_x$  species, the matching of the redox cycles of  $VO_x$ during the reaction was hindered, due to the formation of deeply reduced  $VO_x$  species with a lower oxidation state of +3, which cannot be efficiently re-oxidized by  $CO_2$ . These understandings can provide important contributions to the essential reason of the structural impacts of  $VO_x$  species on  $CO_2$ -ODP, which are beneficial to promote the development of highly active and stable  $VO_x$ -based catalysts for  $CO_2$ -ODP.

## Author contributions

Li Wang: investigation, formal analysis, data curation, visualization, writing – original draft; Heng-Bo Zhang: conceptualization, investigation, formal analysis, data curation; Rong-Rong Hu and Han-Qing Ge: project administration; Guo-Qing Yang: conceptualization, investigation, methodology, writing – review & editing; Yuefeng Li, and Zhao-Tie Liu: investigation; Zhong-Wen Liu: conceptualization, supervision, writing – review & editing.

# Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

# Conflicts of interest

There are no conflicts to declare.

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