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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[†]

vanadium oxides for oxidative dehydrogenation of

Li Wang,^{ab} Heng-Bo Zhang,^a Rongrong Hu, D^a Han-Qing Ge,^a Yong-Hong Song,^a

As an extensively used industrial catalyst for oxidation reactions, supported vanadium oxide (VO_x) is a promising candidate for oxidative dehydrogenation of propane with carbon dioxide (CO₂-ODP). Although the structure of VO_x is found to be a key factor in determining the catalytic activity and stability of supported VO_x for CO₂-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_x species, *i.e.*, monomeric VO_x, less polymeric VO_x, highly polymeric VO_x and V₂O₅ 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_x species decrease in the order of monomeric VO_x > less polymeric VO_x > highly polymeric VO_x > highly polymeric VO_x species by CO₂, which coincides with the ability for the re-oxidation of the reduced VO_x species by CO₂. As a result of the most facile re-oxidation of the reduced

monomeric VO_x species by CO₂, a well matched redox cycle of V^{5+}/V^{4+} oxides during CO₂-ODP can be maintained with increasing the time on stream, leading to an improved stability of the catalyst with more

monomeric VO_x. These mechanistic findings on the redox properties of VO_x with different structures can

Guo-Qing Yang,*^a Yuefeng Li,^b Zhao-Tie Liu^b and Zhong-Wen Liu^{*}

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.^{1,2} However, only the direct propane dehydrogenation (PDH) technologies are commercialized on large scales, which characterize low propene productivity and high energy consumption.^{2,3} To overcome these shortcomings, the oxidative dehydrogenation of propane using carbon dioxide as a soft oxidant (CO₂-ODP) has attracted much attention.^{3,4} In comparison with PDH, CO₂-ODP can promote the equilibrium conversion of propane by removing the produced hydrogen *via* CO₂ reduction. Moreover, CO₂-ODP favors a higher propene selectivity than that by using O₂ as an oxidant due to the soft oxidizing

^a 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

^b Kaili Catalyst & New Materials Co., Ltd, Xi'an 710201, China

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ability of CO₂. Importantly, the efficient production of two valueadded products of propene and CO from propane and the greenhouse gas of CO₂, respectively, turns CO₂-ODP into a charming tandem process from an environmental viewpoint.4,5 Moreover, although the separation of gaseous species resulting from the introduction of CO₂ remains a significant challenge, the CO₂-ODP product mixtures can be directly used as feeds to produce useful chemicals, such as the oxidative coupling of CO₂ 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.⁶ As a result of these advantages, a number of catalysts including supported or bulk metal oxides e.g., Cr,⁷ V,⁸ In,⁹ Ga,¹⁰ and Zn,¹¹ and supported metals, *e.g.*, Pd,¹² and Pt^{13,14} have been extensively studied for CO₂-ODP. Among these potential catalysts, supported vanadium oxides (VO_x) are promising for CO₂-ODP considering their low price, environmental sustainability and competitive catalytic performance.^{2,15} However, the rational design of a high-performance supported VO_x 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_x species.^{16,17} A similar conclusion is also valid for the oxidative dehydrogenation of ethylbenzene with CO₂ reaction, in which monomeric VO_x are more active and more stable than polymeric VO_x and crystalline V₂O₅.¹⁸ Although these observations are tentatively correlated with the structural and chemical properties of VO_x species with different structures, the essential reason in the mechanistic aspect, especially the activation of CO₂ and the balance between the activations of C-O bonds in CO₂ and C-H bonds in C₃H₈ 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.^{8,19} Thus, the redox cycles of the VO_x species participated with CO₂ 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 CO₂ for the simultaneous formation of CO. If the weak oxidizing ability of CO₂ is taken into account, the re-oxidation of V⁴⁺ 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_x species for CO₂-ODP may be closely related to their different abilities for activating and converting CO₂ molecules. However, the detailed mechanistic understandings are still of lacking, and only the partial re-oxidation of the reduced VO_x species by CO₂ is reported.^{20,21}

As a common practice, supported VO_x with the structures of monomeric VO_x, less or highly polymeric VO_x and even crystalline V₂O₅ 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%,^{22–24} which makes it difficult to unambiguously correlate the catalytic performance of VO_x 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 decreased²⁵ and constant²⁶ 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_x structures while narrow V loading distributions are desired for better understanding the essential reason of the VO_x 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.^{27,28} To date, the widely reported methods for preparing supported VO_x catalysts are one-step direct synthesis and impregnation method.^{29,30} 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.³¹ 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.^{32,33}

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 V₂O₅, 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 C₃H₈ molecules induced from different VO_r 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 CO₂ 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 synthesis²⁹ 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 (NH₄VO₃, \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_x-SiO₂-H and 6VO_x-SiO₂-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 SiO₂-supported VO_x catalyst with a V loading of 6 wt%. Before loading VO_x, SiO₂ with a BET surface area of 580 m² g⁻¹ 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 NH₄VO₃ 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 SiO₂-supported VO_x catalyst with a V loading of 6 wt% was also prepared by the physical grinding method. The same SiO₂ support (2 g) to that used in the impregnation experiment was directly blended with 0.275 g of NH₄VO₃ 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 HNO₃ (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 α radiation (Bruker D8 Advance, 40 kV, 40 mA). The sample was scanned from 2θ value of 10° to 80° with a speed of 0.2 s per step.

Raman spectra of the fresh catalysts in the range of 200– 1200 cm⁻¹ 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⁻¹ 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⁻¹) for 40 min. After cooling to ambient temperature in an Ar flow, Raman spectra were collected. The Raman spectra of the spent catalysts for CO₂-ODP were directly recorded in the range of 1100– 1700 cm⁻¹ 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 BaSO₄ (\geq 99.0%, Macklin Biochemical Co. Ltd, Shanghai, China), and then pre-treated at 400 °C under Ar (30 mL min⁻¹) for 40 min. After cooling to room temperature, the spectra were recorded in the range of 200–800 nm by using BaSO₄ 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 H₂ (H₂-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⁻¹). After cooling to 50 °C, the sample was heated from 50 to 800 °C with a rate of 10 °C min⁻¹ in a 10 vol% H₂/Ar flow (30 mL min⁻¹). H₂ 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 α radiation source (1486.6 eV). The C 1s spectrum at 284.6 eV was applied to calibrate the obtained spectra of the samples.

CO₂ pulse experiments were performed on an AutoChem 2950 HP Chemisorption instrument (Micromeritics, USA). 0.25 g of catalyst was pre-reduced by 10 vol% H₂/Ar (30 mL min⁻¹) at 600 °C for 1 h. After purging with Ar (30 mL min⁻¹) for 30 min, pulse of CO₂ (0.5 mL loop) mixed with a flow of Ar (20 mL min⁻¹) passed through the reduced catalyst. The temporal change of CO₂ (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 CO₂ 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⁻¹ in a flow of air (50 mL min⁻¹).

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⁻¹, and then the gas mixture of $Ar/C_3H_8/CO_2$ (32 mL min⁻¹) 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 (CH₄, 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[†]), 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 C₃H₈ via the reforming of propane with CO₂ reaction (CO₂-RP) was estimated by subtracting the sum of the hydrocarbon products (CH₄ + C₂H₄ + C₂H₆ + C₃H₆) 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⁻¹) of C₃H₈, CO₂ and CO, respectively, *i* stands for the detected hydrocarbon product of CH₄, C₂H₆, C₂H₄ or C₃H₆, 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_{initial} and X_{final} is the initial and final conversion of propane or CO₂ 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 $6VO_x$ -SiO₂-H with the highest propane conversion according to ref. 35–37. The detailed calculations are given in Section 12 in the ESI.[†] The calculated C_{WP} of 1.54×10^{-3} and C_{MM} of 2.82×10^{-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/CO₂ 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⁻¹.

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

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

where 22 400, m_{cat} and *c* stand for the molar volume at standard conditions (mL mol⁻¹), catalyst mass (g), and the content of V over the catalyst (mmol g⁻¹), respectively.

3. Results and discussion

3.1. Structural and chemical properties of the catalysts

The amounts of V over the $4VO_x$ -SiO₂-H, $6VO_x$ -SiO₂-H, $6VO_x$ /SiO₂-I and $6VO_x$ /SiO₂-P catalysts were determined by ICP-MS. According to the results given in Table 1, the nominal V loading of $4VO_x$ -SiO₂-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 $4VO_x$ -SiO₂-H and $6VO_x$ -SiO₂-H, only a broad peak at about 22.6° corresponding to the SiO₂ support with amorphous nature was detected, suggesting the presence of highly dispersed VO_x species. Contrary to this, additionally weak reflections at 2θ of 20.3°, 26.2° and 31.1° were observed for $6VO_x$ /SiO₂-I, which are assigned to (001), (110), and (400) crystal planes of crystal-line V_2O_5 , respectively.^{18,22} In the case of $6VO_x$ /SiO₂-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 _x -SiO ₂ -H	4.0	810
6VO _x -SiO ₂ -H	5.7	809
6VO _x /SiO ₂ -I	5.8	518
6VO _x /SiO ₂ -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 H₂-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 $4VO_x$ -SiO₂-H and $6VO_x$ -SiO₂-H catalysts prepared by one-pot hydrothermal synthesis show a higher dispersion of VO_x .

Textural properties of the catalysts were analyzed by N₂ adsorption–desorption isotherms. As given in Fig. S2a (ESI[†]), all catalysts exhibited the similar type-IV isotherms with an H1-type hysteresis loop, which are typical characteristics of the capillary condensation of N₂ 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[†]). From the calculated textural parameters summarized in Table 1, the specific surface areas of $4VO_x$ -SiO₂-H and $6VO_x$ -SiO₂-H were about ~ 800 m² g⁻¹, which are clearly higher than that of $6VO_x/SiO_2$ -I and $6VO_x/SiO_2$ -P (~ 500 m² g⁻¹). This commonly leads to a higher dispersion of VO_x, 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_x species, while the latter shows a higher sensitivity to crystalline V₂O₅.^{22,23,38} As shown in the Fig. 1b, two UV Raman bands at ~ 460 and 1030 cm⁻¹ 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.³⁸⁻⁴⁰ However, an additionally weak Raman band at 994 cm⁻¹ was detected for 6VO_x/SiO₂-I and 6VO_x/SiO₂-P, indicating the presence of crystalline V_2O_5 .^{22,41} This can be more clearly reflected by the visible Raman spectra as given in Fig. 1c. Only the Raman band at ~ 1035 cm⁻¹ and the weak and broad band at about 484 cm⁻¹ assigned to V=O vibration and the SiO₂ support,^{38,40} respectively, were observed in the spectra of 4VO_x-SiO₂-H and 6VO_x-SiO₂-H. However, the Raman bands at 273, 398, 472, 514, 686, and 994 cm⁻¹ assigned to crystalline V₂O₅ were clearly observed in the case of 6VO_x/SiO₂-I.⁴⁰ Furthermore, the intensity of these Raman bonds becomes more pronounced in the spectrum of 6VO_x/SiO₂-P, accompanying an almost disappearance of V \equiv O vibration at 1035 cm $^{-1}$. This suggests the formation of dominated crystalline V2O5 over 6VO_x/SiO₂-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_x 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.^{31,44} The bands at 325 and 385 nm are generally assigned to oligomeric VO_r species in either tetrahedral or octahedral coordination environment.37,45 Additionally, the octahedral V₂O₅ crystallites can be observed at \sim 510 nm.^{37,45} For $4VO_x$ -SiO₂-H, the strongest bonds at 222 and 243 nm were observed. However, the intensity of these two bonds was decreased over 6VO_x-SiO₂-H, accompanying the enhanced signals at 325 and 385 nm. This indicates that the 4VO_x-SiO₂-H catalyst shows the most isolated VO_x species, while more polymeric VO_r was formed over $6VO_r$ -SiO₂-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 V₂O₅. As for 6VO_x/SiO₂-P, the intensity of the band at 510 nm became more pronounced, suggesting the presence of higher amount of crystalline V₂O₅.

Furthermore, the edge energy (E_g) of these catalysts was determined based on the UV-Vis DRS results. As shown in Fig. S3 (ESI[†]) and 1e, the calculated E_g decreased in the order of 4VO_x-SiO₂-H (3.48 eV) > 6VO_x-SiO₂-H (3.32 eV) > 6VO_x/ SiO₂-I (2.90 eV) > 6VO_x/SiO₂-P (2.50 eV), indicating an increased degree of polymerization or domain size of VO_x.^{18,24} Moreover, the E_g for 4VO_x-SiO₂-H was very close to that for the bulk Na₃VO₄ (3.55 eV) only consisting of isolated VO_x species.⁴⁶ Thus, the isolated VO_x species was dominated over 4VO_x-SiO₂-H. However, in the case of 6VO_x/SiO₂-P, the E_g was comparable with that of the bulk V₂O₅ (2.33 eV),⁴⁶ suggesting the presence of dominated crystalline V₂O₅.

To study the redox property of the VO_x species over the catalysts, H₂-TPR was performed. As shown in Fig. 1f, only a reduction peak at around 530 °C was observed for $4VO_x$ -SiO₂-H and $6VO_x$ -SiO₂-H, which can be easily assigned to the reduction of highly dispersed VO_x species.^{47,48} 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_x species, while the weak peak at 624 °C can be attributed to the reduction of a small

amount of microcrystalline V₂O₅.⁴⁹ In the case of 6VO_x/SiO₂-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_x species, while two sharp peaks at higher temperatures originate from the different stages for the reduction of bulk V₂O₅ from V⁵⁺ to V⁴⁺, and then to V^{3+,50} Moreover, the continuously increased peak temperatures in the order of 4VO_x-SiO₂-H (528 °C) < 6VO_x-SiO₂-H (536 °C) < 6VO_x/SiO₂-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_x species.^{29,49}

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 V⁵⁺ is dominated species on the catalysts surface.^{18,22} Taking this fact and the total amounts of H₂ consumption during H₂-TPR into account, the average oxidation state (AOS) of V over different catalysts after H₂-TPR was calculated. As given in Table 2, the AOS of V decreased in the order of $4VO_x$ -SiO₂-H (+4.06) < $6VO_x$ -SiO₂-H (+3.88) < $6VO_x$ /SiO₂-I (+3.62) < $6VO_x$ /SiO₂-P (+3.35). This indicates that the reduction degree of VO_x species increases with increasing its polymerization degree or domain size, leading to a more favorable reduction of V⁵⁺ to V³⁺ instead of V^{4+.18,22}

Based on these complementary characterizations, the dominated structures of VO_x over the four catalysts are proposed and illustrated in Scheme 1. It can be concluded that (1) monomeric VO_x species is dominantly present over $4VO_x$ -SiO₂-H; (2) monomeric and less polymeric VO_x coexist over the $6VO_x$ -SiO₂-H catalyst; (3) highly polymeric VO_x and a small amount of crystalline V₂O₅ are present over $6VO_x/SiO_2$ -I; and (4) crystalline V₂O₅ 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 $6VO_x$ -SiO₂-H > $4VO_x$ -SiO₂-H > $6VO_x$ /SiO₂-I > $6VO_x$ /SiO₂-P. If the CO₂ 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 $4VO_x$ -SiO₂-H > $6VO_x$ -

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

^{*a*} Calculated based on the H₂-TPR results as given in Fig. 1f. ^{*b*} Cumulative amount of CO formed from the pulse of CO₂ over the reduced catalyst at 600 $^{\circ}$ C as given in Fig. 4a–d.



Scheme 1 Illustration of the dominated VO_x species over 4VO_x-SiO₂-H (a), 6VO_x-SiO₂-H (b), 6VO_x/SiO₂-I (c) and 6VO_x/SiO₂-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⁻¹, and GHSV = 7680 mL g⁻¹ h⁻¹.

SiO₂-H > 6VO_x/SiO₂-I » 6VO_x/SiO₂-P. To understand the main side reactions, the initial selectivity of gaseous by-products was analyzed. As shown in Fig. 2c, CH₄, C₂H₄ and C₂H₆ originating from the cracking and CO produced from the CO₂-RP reaction were detected. For all catalysts, the total selectivity for the byproducts of CH₄, C₂H₄ and C₂H₆ was centered at around 5%. However, the selectivity of CO increased from 7.6% to 26.0% in the order of 4VO_x-SiO₂-H < 6VO_x-SiO₂-H < 6VO_x/SiO₂-I « 6VO_x/SiO₂-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 $4VO_x$ -SiO₂-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 V₂O₅. A similar result is observed in the chemical looping oxidative dehydrogenation of propane catalyzed by VO_x/TiO₂, suggesting that the highly dispersed VO_x is the main active species for the oxidative dehydrogenation of propane.⁵¹

In the case of the catalytic stability, an apparently decreased conversion of either propane or CO₂ with increasing TOS was observed for all catalysts (Fig. S5a and b, ESI[†]). To quantitatively estimate the stability of the catalysts, the relative deactivation rate associated with propane conversion was calculated (R_{propane} , see eqn (6)). As given in Fig. 2d, the stability of the catalysts varied in a lager extent, and R_{propane} increased in the order of 4VO_x -SiO₂-H < 6VO_x -SiO₂-H < 6VO_x /SiO₂-I < 6VO_x /SiO₂-I < 6VO_x /SiO₂-F. The same change pattern was observed when the relative deactivation rate was calculated based on the CO₂ conversion (R_{CO_2} , Fig. S6, ESI[†]), resulting in the best stability of the 4VO_x-SiO₂-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_{α} , 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 $4VO_x$ -SiO₂-H with dominantly monomeric VO_x. In the case of the 4VO_x-SiO₂-H and 6VO_x-SiO₂-H catalysts, no crystalline V₂O₅ can be detected, and only two-dimensional VO_x species is present. Moreover, the textural properties of 4VO_x-SiO₂-H and 6VO_x-SiO₂-H, *i.e.* the surface area and pore size distributions are almost the same (Table 1 and Fig. S2, ESI[†]), which commonly leads to the very similar V distributions on the SiO₂ support. Thus, the decreased $TOF(C_3H_8)$ can be ascribed to the increased in the polymerization degree of VO_x .^{16,17} However, the crystalline V_2O_5 is formed



Fig. 3 Relationship between TOF(C₃H₈) and E_{g} derived from UV-vis DRS of the catalysts.

over the 6VO_x/SiO₂-I and 6VO_x/SiO₂-P catalysts, in which not all V atoms can be touched with the reactants during the reaction. Thus, the decreased TOF(C₃H₈) from 6VO_x/SiO₂-I to 6VO_x/SiO₂-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_r illustrated in Scheme 1 indicate that the activity of VO_x species for CO₂-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_{α} (Fig. S7, ESI[†]), exactly the same change pattern to that of the $TOF(C_3H_8)$ was observed, and the highest value was obtained over 4VO_x-SiO₂-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.⁵²

According to the Mars-van Krevelen redox mechanism for CO₂-ODP catalyzed by supported VO_x catalysts,^{8,53} the activated propane molecules abstract the active oxygen from the VO_r species with a high V oxidation state (+5) to produce propene and water. Simultaneously, VO_x 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 CO₂ 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 CO₂ 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 CO₂ (m/z = 44) was pulsed, CO (m/z = 28) was detected over all the catalysts pre-reduced by H₂. Moreover, for pure SiO₂ support prepared by hydrothermal synthesis method, no CO signal (m/z = 28) was detected (Fig. S8, ESI⁺). These results indicate that the reduced VO_x 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 μ mol $g_{catalyst}^{-1}$ in the order of $6VO_x$ -SiO₂-H > $4VO_x$ -SiO₂-H > $6VO_x$ /SiO₂-I > $6VO_x$ /SiO₂-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 $4VO_x$ -SiO₂-H > $6VO_x$ -SiO₂-H > $6VO_x$ /SiO₂-I > 6VO_x/SiO₂-P. Thus, the re-oxidized ability of the reduced catalysts by CO₂ decreases with increasing the polymerization extent or domain size of VO_x over the parent catalysts, and $4VO_x$ -SiO₂-H with dominantly monomeric VO_x 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 V⁵⁺ 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 CO₂ 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 CO₂ pulse experiments.

other hand, the CO₂ pulse experiments were performed at 600 °C, however the 6VO_x-SiO₂-P catalyst, which exhibits a reduction peak at a higher temperature of about 700 °C during H₂-TPR, may not be fully reduced at 600 °C. This also led to a lower amount of released CO when CO₂ was pulsed. Moreover, the amount of released CO (270 µmol g_{catalyst}⁻¹) during the CO₂ pulse experiments over 4VO_x-SiO₂-H with the best ability for the activation of CO₂ is still lower than the amount of H₂ consumption (358 µmol g_{catalyst}⁻¹) during the H₂-TPR (Table 2). This indicates that the reduced VO_x species cannot be fully reoxidized by CO₂ owning to the weak oxidizing ability of CO₂.

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

with the amount of formed CO per gram of catalyst (mmol $g_{catalyst}^{-1}$) determined by CO₂ 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 < $4VO_x$ -SiO₂-H < $6VO_x$ -SiO₂-H with increasing the amount of formed CO. The higher amount of formed CO during the CO₂ pulse experiments means the supplement of more active oxygen species over the reduced catalysts by CO₂ reduction. Thus, this result clearly indicates that the activity of the parent catalyst is determined by the ability in activating CO₂ 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_x and the catalytic activity, the TOF(C₃H₈) 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(C₃H₈) increased in the order of $6VO_x/SiO_2$ -P $< 6VO_x/SiO_2$ -I $< 6VO_x$ -SiO₂-H $< 4VO_x$ -SiO₂-H. The reduced $4VO_x$ -SiO₂-H catalyst with dominantly monomeric VO_x species is the most easily reoxidized by CO₂, thereby the parent catalyst can well complete the redox cycle of VO_x during CO₂-ODP, resulting in the highest TOF(C₃H₈).

3.4. Insight into the catalytic stability

Generally, the coke deposition on the catalyst surface during the CO₂-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[†]). 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⁻¹, assigning to the disordered (D band) and graphitic carbon (G band),^{16,56} 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 $(I_{\rm D}/I_{\rm G})$.^{16,56} As given in Table 3, the $I_{\rm D}/I_{\rm G}$ was determined as 0.74 ± 0.08 for $4VO_x$ -SiO₂-H, $6VO_x$ -SiO₂-H and $6VO_x$ /SiO₂-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_x/SiO₂-P, indicating the highest graphitization extent of coke species.^{7,16,56} As revealed from the analyses of the by-product selectivity, the 6VO_x/SiO₂-P catalyst with dominated V₂O₅ is the most favorable to break C-C bond via the CO2-RP and cracking reactions, while the remaining catalysts are more promising for CO₂-ODP. Thus, the highest graphitization extent of coke species over 6VO_x/SiO₂-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.⁵⁷ Additionally, the coke content decreased in the order of $6VO_r$ -SiO₂-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⁻¹) over the catalyst for CO₂-ODP was calculated. As given in Table 3, the coking rate was determined as 0.45 \pm 0.03 g mol⁻¹ for $4VO_x$ -SiO₂-H, $6VO_x$ -SiO₂-H and $6VO_x$ /SiO₂-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⁻¹ 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 CO₂-ODP after a TOS of 128 min

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

^{*a*} Determined by the TG results as given in Fig. S9 (ESI). ^{*b*} Calculated based on the visible Raman results as given in Fig. S10 (ESI). ^{*c*} Calculated based on the amount of the coke by converting 1 mol propane. ^{*d*} 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_{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 CO₂-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_{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_x species into account, the V⁵⁺ 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 CO₂ to V⁵⁺ to complete the redox cycles.^{18,54} Thus, the deep reduction of V⁵⁺ to V³⁺ during the reaction may be associated with the catalyst deactivation. To confirm this, the spent catalysts after CO₂-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^{\dagger}), indicating an increased content of VO_x with a lower oxidation state^{18,22} after the CO₂-ODP reaction. To make a quantitative comparison, the V 2p_{3/2} spectra were deconvoluted. As given in Fig. 5b, three peaks at 515.7, 516.6 and 517.6 eV assigned to V³⁺, V⁴⁺ and V⁵⁺ species,^{22,58} 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 $4VO_x$ -SiO₂-H > $6VO_x$ -SiO₂-H > $6VO_x$ /SiO₂-I > $6VO_x$ /SiO₂-P, the change pattern is consistent with that of their catalytic stability, *i.e.*, the higher content of V⁵⁺ remained on the spent catalyst surface, the better stability of the catalyst was (Fig. S11a, ESI⁺). Contrary to this, when the relative fraction of V³⁺ 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 CO₂ pulse experiments (a), and V $2p_{3/2}$ XP spectra of the spent catalysts after CO₂-ODP for a TOS of 128 min (b).

was found (Fig. S11b, ESI[†]). 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 CO₂-ODP. Thus, the redox rates of the VO_x species participated with CO₂ and propane are not very well matched, owning to the weak oxidizing ability of CO₂. This is consistent with the CO₂ pulse experiments and H₂-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 $4VO_x$ -SiO₂-H, the best performance for CO_2 -ODP was obtained among the evaluated catalysts.

4. Conclusions

In summary, four SiO₂-supported VO_x catalysts with narrow distributions of V loading while well-defined structures of VO_x species were synthesized by applying appropriate preparation methods. The dominated monomeric and less polymeric VO_x were formed over the 4VO_x–SiO₂-H and 6VO_x–SiO₂-H catalysts, respectively, prepared by one-pot hydrothermal synthesis. In case of the 6VO_x/SiO₂-I catalyst prepared by simply impregnation method, the highly polymerized VO_x with a small amount of V₂O₅ was present, while V₂O₅ crystallites were overwhelmingly predominant over the 6VO_x/SiO₂-P catalyst prepared by physic grinding method. The catalytic activity and stability for CO₂-ODP decreased in the order of 4VO_x–SiO₂-H > 6VO_x–SiO₂-I > 6VO_x/SiO₂-P, which can be explained



Scheme 2 Redox mechanism over supported VO_x catalyst for CO₂-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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