

CO₂-Assisted Oxidative Dehydrogenation of Propane over VO_x/In₂O₃ Catalysts: Interplay between Redox Property and Acid–Base Interactions

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Cite This: *ACS Catal.* 2022, 12, 11239–11252



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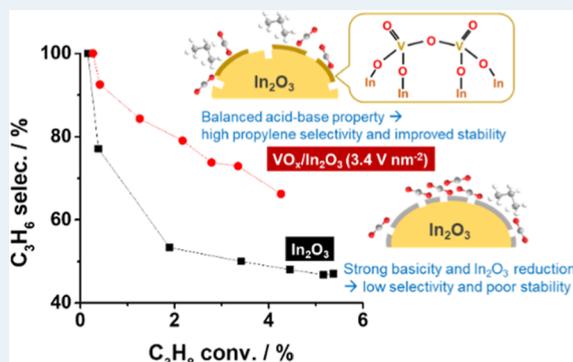
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Supporting Information

ABSTRACT: In this work, a series of VO_x-loaded In₂O₃ catalysts were prepared, and their catalytic performance was evaluated for CO₂-assisted oxidative dehydrogenation of propane (CO₂-ODHP) and compared with In₂O₃ alone. The optimal composition is obtained on 3.4V/In₂O₃ (surface V density of 3.4V nm⁻²), which exhibited not only a higher C₃H₆ selectivity than other V/In catalysts and In₂O₃ under isoconversion conditions but also an improved reaction stability. To elucidate the catalyst structure–activity relationship, the VO_x/In₂O₃ catalysts were characterized by chemisorption [NH₃-temperature-programmed desorption (TPD), NH₃-diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), CO₂-TPD, and CO₂-DRIFTS], H₂-temperature-programmed reduction (TPR), in situ Raman spectroscopy, UV–vis diffuse reflectance spectroscopy, near-ambient pressure X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and further examined using density functional theory. The In–O–V structure and the extent of oligomerization, which play a crucial role in improving selectivity and stability, were identified in the VO_x/In₂O₃ catalysts. In particular, the presence of surface VO_x (i) inhibits the deep reduction of In₂O₃, thereby preserving the activity, (ii) neutralizes the excess basicity on In₂O₃, thus suppressing propane dry reforming and achieving a higher propylene selectivity, and (iii) introduces additional redox sites that participate in the dehydrogenation reaction by utilizing CO₂ as a soft oxidant. The present work provides insights into developing selective, stable, and robust metal-oxide catalysts for CO₂-ODHP by controlling the conversion of reagents via desired pathways through the interplay between acid–base interactions and redox properties.

KEYWORDS: oxidative dehydrogenation, propane, carbon dioxide, indium oxide, vanadium oxide, acid–base interaction, redox property



1. INTRODUCTION

Light alkenes such as propylene (C₃H₆) are important building blocks for a large number of chemicals in the petrochemical industry.¹ Conventionally, C₃H₆ is produced as a byproduct in producing ethylene by steam cracking and fluid catalytic cracking of naphtha, light diesel, and other oil byproducts.² Nowadays, there is a discrepancy between the market demand and productivity.³ To make-up the shortfall of C₃H₆ supply, the on-purpose C₃H₆ production technologies such as dehydrogenation of propane (DHP) have been implemented.^{2,4,5} However, DHP suffers from intrinsic drawbacks such as thermodynamic restraints which require high reaction temperatures that inevitably result in severe coking and undesired thermal cracking.⁶ Moreover, the indispensable addition of extra hydrogen in the feed gas and its regeneration make the process both energy and capital intensive.^{7–10}

Due to its exothermicity and limited thermodynamic restraint, oxidative dehydrogenation of propane (ODHP)

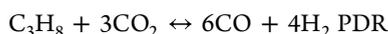
provides alternatives to complement the DHP route.¹¹ Presently, oxygen (O₂) has been majorly used as the oxidant for ODHP, and higher C₃H₆ and light alkene (C₂–C₃) selectivities can be achieved. Representative catalysts include hexagonal boron nitride and boron oxide catalysts through the Eley-Rideal (ER) mechanism^{12–18} and redox-active vanadium oxide-based catalysts via a Mars-van Krevelen mechanism (MvK).¹ Over-oxidation to undesired carbon oxides (CO_x) is the major challenge with O₂ as the oxidant, which reduces the selectivity toward alkenes.^{1,19} Furthermore, concerns of process flammability due to the presence of O₂ also

Received: April 28, 2022

Revised: August 23, 2022

exist.^{11,20} To tackle these issues, introducing a soft oxidant such as carbon dioxide (CO₂) provides a potential avenue and has been applied in the coupling of methane,²¹ dehydrogenation of ethylbenzene,²² propane,^{11,23} and iso-butane.²⁴ The positive roles of CO₂ in the overall ODHP reaction include serving as (i) a diluent to enhance the equilibrium conversion of light alkanes and (ii) an agent to remove coke via the reverse Boudouard reaction.²⁵ Moreover, CO₂ can help keep the metal components at a higher oxidation state during CO₂-ODHP, such as inhibiting the formation of metallic iron and iron carbide with better activity toward isobutane dehydrogenation.²⁶ Combining CO₂ with the ODHP reaction can also potentially allow for the utilization of the carbon source from CO₂ via a hydrogen-free manner.¹¹

In addition to ODHP, side reactions include reverse water gas shift (RWGS) and propane dry reforming (PDR) (see reactions below).^{11,23,27} There are two proposed reaction cycles. The first scenario proposes that CO₂-ODHP is a net reaction of DHP and RWGS, wherein RWGS can help remove the formed H₂ to form CO and H₂O, therefore boosting the DHP reaction by shifting the reaction equilibrium to the side of forming propylene.^{11,28} Alternatively, the reaction can proceed through a one-cycle reaction, in which CO₂ closes the cycle to produce CO without undergoing a separate RWGS route after the surface undergoes direct propane dehydrogenation.²⁹ PDR is endothermic, which could result in the increase in CO while a decrease in C₃H₆ selectivity at high temperatures. Therefore, designing catalysts that can selectively break the C–H bond to produce alkenes while suppressing PDR is of great interest. Similar to the O₂-ODHP route, redox-active metal oxides (Cr and V) are promising candidates for CO₂-ODHP.^{1,11,30} However, due to the toxic and carcinogenic properties of Cr(VI) oxides, it is vital to find alternatives.³⁰ Group IIIA mixed oxides such as Ga₂O₃–Al₂O₃^{31,32} and In₂O₃–Al₂O₃³³ and supported In₂O₃ catalyst^{25,34} show comparable catalytic performance as well. On Ga₂O₃, ODHP is proposed to proceed via the heterolytic propane dissociation on acid–base pairs, namely, Ga^{δ+}–O²⁻ pairs.²⁸ Specifically, C₃H₇⁺ is adsorbed on O₂⁻ (basic sites), while H⁻ is adsorbed on Ga^{δ+} (acid sites).²⁸ The presence of CO₂ aids in facilitating the removal of dissociatively adsorbed H₂ on acid–base pairs of Ga–O and recovering the active sites for the subsequent C–H activation for propylene formation.²⁸



Our interest lies in the In₂O₃-based catalysts because of their comparable C₃H₆ selectivity to Ga₂O₃ under isoconversional conditions¹¹ and well-known capability in activating CO₂ molecules, such as CO₂ hydrogenation.^{35–38} However, the mechanism on In₂O₃ for ODHP is still elusive. CO₂ is a more acidic gas than propane, which might negatively impact the C–H activation of C₃H₈ during ODHP.²⁸ Thus, due to the strong basicity of In₂O₃,^{35–38} it might selectively activate CO₂ instead of C₃H₈ during ODHP. Thus, the unbalanced acid–base properties of In₂O₃ is a major challenge for ODHP.¹¹ In the present work, we propose to incorporate an acidic metal oxide VO_x onto the basic In₂O₃ to (i) neutralize the excess basic sites (oxygen vacancies and lattice oxygen) with controlled capability of CO₂ activation and to (ii) improve the reaction

stability through the intimate interaction between In₂O₃ and redox-active VO_x. Thus, we aim at clarifying the interplay between redox property and acid–base interactions and their relationship with the activity performance and stability in CO₂-ODHP. For these purposes, we prepared a series of VO_x-loaded In₂O₃ catalysts with various surface V densities and evaluated their catalytic performance in CO₂-ODHP. To reveal the catalyst composition–structure–activity relationship, a wide array of the characterization techniques has been applied, including chemisorption, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), X-ray absorption spectroscopy (XAS), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), and Raman spectroscopy. Density functional theory (DFT) was also used to study the effect of surface VO_x on the formation of oxygen vacancies of In₂O₃.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. In₂O₃ (surface area, ~70 m² g⁻¹) was prepared by the calcination of In(OH)₃, as reported elsewhere.³⁵ A brief description is provided in the [Supporting Information](#). The crystalline V₂O₅ was prepared by calcining the precursor NH₄VO₃ at 550 °C. The structure of V₂O₅ was characterized by Raman spectroscopy, and the resultant spectrum is shown in [Figure S1](#).

V-loaded In₂O₃ catalysts were prepared by impregnation in an aqueous solution of NH₄VO₃ (99.0%, Sigma-Aldrich) at 80 °C for 4 h with vigorous stirring. The impregnated sample was dried at 100 °C overnight and calcined in air at 550 °C for 3 h at a ramp rate of 5 °C min⁻¹. V surface density is used throughout the work, wherein the V loading [determined by ion-coupled plasma-optical emission spectroscopy (ICP-OES)] was normalized to the surface area of In₂O₃ ([Table S1](#)). Catalysts were denoted as *x*V/In, wherein *x* represents the surface V density and varies from 0 to 5.6V nm⁻².

2.2. Activity Tests. The following pre-mixed gas cylinders were purchased from airgas and used for activity tests, including 5% C₃H₈/He and 2% CO₂/Ar. The activity test of the CO₂-ODHP reaction was performed using an Altamira Instruments system (AMI-200). Typically, 100 mg of the catalyst was diluted with 600 mg of quartz sand (60–80 mesh). The mixture was loaded in a quartz U-tube (i.d. = 10 mm) with quartz wool at both ends of the mixture. Prior to the activity test, 2% CO₂/Ar was introduced to pretreat the catalyst at 500 °C for 1 h under 30 mL min⁻¹. Then, the catalyst bed was cooled to the desired temperature. The activity test was initiated by switching to the reaction gas consisting of C₃H₈, CO₂ and balanced with He/Ar (C₃H₈/CO₂ = 1) with weight hourly space velocity (WHSV) = 18000 mL g⁻¹ h⁻¹. The reaction was conducted in the temperature range of 350–540 °C, and each reaction temperature was maintained for 2 h.

Compositions of effluent gas were analyzed periodically using an online SRI 8610C gas chromatograph equipped with both thermal conductivity detector (TCD) and flame ionization detector (FID) detectors. MTX-WAX and Molecular Sieve 5A columns were attached to the TCD detector, analyzing CO and CO₂, while HayeSep-D and alumina were attached to the FID detector, analyzing hydrocarbons including C₃H₈, C₃H₆, C₂H₆, C₂H₄, and CH₄. A mass spectrometer (Pfeiffer Vacuum) was also coupled with GC to monitor the real-time fragments of reactants and products in the effluent gas. Conversion and selectivity were calculated

based on the reported methods (see Section S3 in Supporting Information).^{39,40}

To study the coking on spent catalysts, stability tests were run at 540 °C for ca. 10 h. The spent catalyst bed was flushed with Ar in 30 mL min⁻¹, and the temperature was cooled to 50 °C. Then, the temperature-programmed oxidation (TPO) experiment was performed using either 2.5% O₂/He or 2% CO₂/Ar (40 mL min⁻¹). The temperature was ramped up to 730 °C at a rate of 10 °C min⁻¹ and maintained for 0.5 h. The generated CO₂ or CO from the outlet was recorded by an OmniStar mass spectrometer (MS) (Pfeiffer Vacuum).

For kinetic studies, compositions were altered by varying the flow rates of 5% C₃H₈/He, 2% CO₂/Ar, and Ar with a constant total flow rate of 40 mL min⁻¹. All reactions were conducted at 500 °C where the conversion is below 10%, and the reduction of bulk In₂O₃ is limited according to H₂-temperature-programmed reduction (H₂-TPR) results. Of note, all flow rates in the present work are normal temperature and pressure (NTP)-based.

2.3. Characterization. Elemental analysis was performed using ICP-OES on a PerkinElmer Avio 500 model instrument. The thermal stability of the catalysts was performed by TGA/DTG analysis using a TA Instruments SDT Q50 instrument. Prior to ramping up the temperature, each sample was pretreated with 25 mL min⁻¹ N₂ flow at 30–35 °C for 1 h to stabilize. Afterward, the sample was heated to 600 °C at a ramp rate of 5 °C min⁻¹ with 25 mL min⁻¹ N₂. Such a process was recycled three times.

NH₃-temperature-programmed desorption (TPD), CO₂-TPD, and TPR were performed using AMI 200. ~50 mg of the fresh catalysts was charged into a U tube for all measurements, except V₂O₅ (~40 mg) for H₂-TPR. In NH₃-TPD, the catalyst was pretreated in 2% CO₂/Ar at 500 °C for 1 h. Then, the system was flushed in Ar, and the temperature was cooled to 120 °C. NH₃ adsorption (2% NH₃/He) was carried out for 1 h (30 mL min⁻¹), followed by Ar flush at 30 mL min⁻¹ for 1 h. TPD was then initiated from 120 to 730 °C (5 °C min⁻¹) in Ar (30 mL min⁻¹) and maintained for 0.5 h. In CO₂-TPD, after similar pretreatment, CO₂ adsorption (2% CO₂/Ar, 30 mL min⁻¹) was performed at 140 °C for 1 h, followed by Ar flush and cooling to 50 °C. TPD was initiated from 50 to 620 °C (5 °C min⁻¹) in Ar (30 mL min⁻¹) and maintained for 0.5 h. In H₂-TPR, the pretreated catalyst bed was cooled to 50 °C prior. Then, the catalyst was reduced in 4% H₂/Ar (30 mL min⁻¹) ramping from 50 to 830 °C (5 °C min⁻¹) and maintained for 1 h. For both NH₃- and CO₂-TPD measurements, the effluent gas was recorded using the same mass spectrometer as TPO and activity tests. The TCD detector was used to record the H₂ signals, and a cooling trap was applied prior to the detector to trap moisture.

The NH₃ adsorption-DRIFTS experiment was performed using a Thermo Nicolet Nexus 670 FT-IR spectrometer with an MCT detector. Each spectrum was acquired with 32 scans at a resolution of 4 cm⁻¹. The sample was loaded in a ceramic cup, and a DRIFTS cell (Pike Technologies) was used. In the experiment, the catalyst was pretreated at 500 °C in 2% CO₂/Ar (30 mL min⁻¹) for 1 h. The system was then cooled to 400, 300, and 200 °C in Ar (30 mL min⁻¹), and corresponding spectra were collected as background references. The system was then cooled to 120 °C and flushed with Ar for 1 h. The NH₃ adsorption was performed at 120 °C using 1% NH₃/Ar/He (30 mL min⁻¹) for 30 min, followed by Ar flushing for 30 min (30 mL min⁻¹) to remove physisorbed NH₃. The

temperature was then heated up sequentially to 200, 300, and 400 °C at a ramp of 10 °C min⁻¹ in Ar. At each temperature, the spectra were continuously recorded every 30 s. The CO₂-DRIFTS experiment was performed using the same equipment by following a similar procedure. 2% CO₂/Ar was used during CO₂-DRIFTS (30 mL min⁻¹). The temperature was elevated to 200, 300, 400, 500, and 550 °C at a ramp of 10 °C min⁻¹. The spectra were processed by using the background spectra acquired at corresponding temperatures.

The content and oxidation states of surface region VO_x species were monitored by NAP-XPS. Spectra of the VO_x-loaded In₂O₃ catalyst were acquired with a SPECS DeviSim NAP reactor coupled with a PHOIBOS 150 NAP electron energy analyzer equipped with a XR 50 MF Al K α X-ray source (1486.7 eV). The sample was prepared by pressing the powder onto a SS 316 steel mesh by applying 5 MPa for 5 min. The pressed sample was then loaded onto a stainless-steel sample holder with a type K thermocouple enabling online measurement of the sample temperature as it was heated using an e-beam heater. The spectra were acquired with a 0.05 eV resolution and were repeated several times to reduce the noise-to-signal ratio. All gasses were flowed as to maintain a pressure of ~1 mbar in the NAP reaction cell. The resulting spectra were processed using CasaXPS (version 2.3.22PR1.0). Due to the lack of a strong C 1s spectra after the initial in situ oxidation of the catalyst, the O 1s spectra were used for binding energy correction. While some contribution by the VO_x species existed, In₂O₃ contributed the bulk of the O 1s signal, resulting in a reliable means of correction. The possible reduction of the In in the surface region was checked for by monitoring the In Auger spectra.⁴¹ The V oxidation states were quantified by analyzing only the V 2p_{3/2} spin-orbit split core spectra due to the weak intensity of the V 2p_{1/2} spin-orbit split core spectra. Previously established binding energies, Lorentzian–Gaussian mixing ratios, and relative full width at half maximum (fwhm) values were applied for the V 2p_{3/2} oxidation state quantification.⁴² Consecutive treatments were carried out at 500 °C for 1 h at a time in the following sequence: 10% O₂/Ar, 5% CO₂/Ar, 2.5% C₃H₈/2.5% CO₂/Ar, 5% CO₂/Ar, and 5% C₃H₈/Ar. There is no regeneration between steps, and these measurements are continuous.

In situ Raman scattering for the samples under reaction conditions was collected on a multiwavelength Raman system using 532 nm laser excitation. Raman scattering was collected via a customized ellipsoidal mirror and diffracted by a fiber optics bundle to the spectrograph stage of a triple Raman spectroscopy (Princeton Instruments Acton Trivista 555). An edge filter (Semrock) was used in front of the UV–vis fiber optic bundle (Princeton instruments) to block the laser irradiation. A neutral density filter was used to attenuate the laser power to 20%, less than 10 mW at the sample position. An UV-enhanced liquid N₂-cooled CCD detector (Princeton Instrument) was used to detect signals. The Raman catalytic reactor (Linkam CCR1000) was placed on an XY stage (Princeton Scientific, OptiScan XY system). During acquisition, the stage translates in a raster mode, which can provide the information of heterogeneity of the samples. The fast translation and the attenuated laser power are also able to minimize the laser damage of the sample. In the experiment, catalysts were pretreated in situ in the Raman reactor before Raman spectral collection at 120 °C. The pretreatment was carried out by heating the sample in 2% CO₂/Ar (30 mL min⁻¹) at 500 °C (ramping rate 10 °C min⁻¹) and held for 30

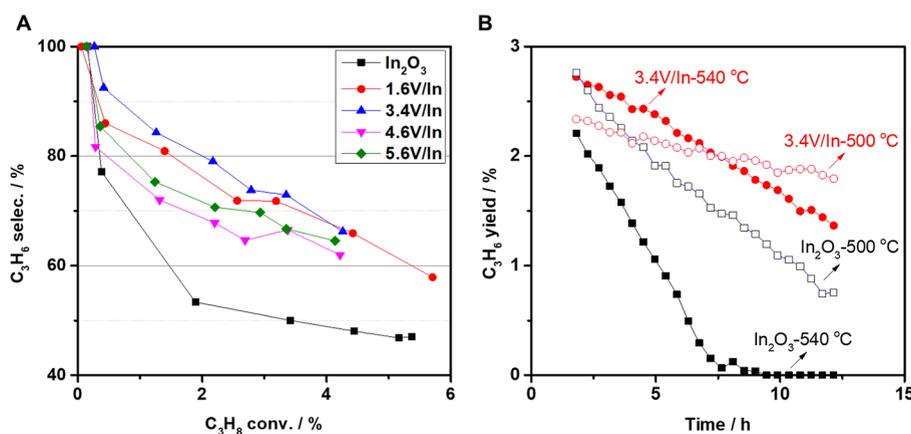


Figure 1. (A) Propylene selectivity-propane conversion plot over $\text{VO}_x/\text{In}_2\text{O}_3$ catalysts with various surface V densities. Reaction conditions: 350–540 °C, ambient pressure, $\text{C}_3\text{H}_8/\text{CO}_2 = 1$, and $\text{WHSV} = 18000 \text{ mL g}^{-1} \text{ h}^{-1}$. (B) Stability on 3.4V/In and In_2O_3 at 500 and 540 °C with similar WHSV and gas compositions.

min. In the reaction, the pretreated catalyst experienced consecutive treatments in CO_2 , $\text{C}_3\text{H}_8/\text{CO}_2$ (1/1), and CO_2 again at 500 °C. The Raman spectra of dehydrated catalysts were acquired at a different Raman system, and the detailed procedures are described in the [Supporting Information](#).

UV–vis DRS measurements were performed in the 200–800 nm range with an Agilent Cary 5000 UV–vis and NIR spectrophotometer. Polytetrafluoroethylene powder (35 μm , Sigma-Aldrich) was used as a reflectance standard. $\text{VO}_x/\text{In}_2\text{O}_3$ catalysts were thoroughly mixed with silica at a 1:1 weight ratio to overcome the sample's signal nonlinearity with intensity. Fumed silica (Cab-O-Sil EH-5, Cabot) was first hydrated with Milli-Q ultrapure water and then dried under 100 mL min^{-1} of dry air (AI D300, Airgas) for 16 h. A heating/cooling rate of 10 °C min^{-1} was used throughout. After crushing with an agate mortar and pestle, the silica was calcined at 500 °C for 4 h under 100 mL min^{-1} of air. The silica-diluted $\text{VO}_x/\text{In}_2\text{O}_3$ samples were loaded into a reaction cell (Harrick Scientific HVC-DR2) and connected to a gas flow control system. A Harrick ATC temperature controller unit controlled the catalyst temperature. Dehydration was performed under 10% O_2/Ar (airgas, 30 mL min^{-1}) as samples were heated to 500 °C and held for 30 min, followed by cooling to 120 °C where the dehydrated spectra were taken. The spectra were acquired with 1 nm resolution and a dwell time of 1.5 s (a scan rate of 40 nm min^{-1}) while using a double beam mode with full slit height and a slit beam width of 2 nm. The surface VO_x direct band gap was determined using the Kubelka–Munk formalism to convert the reflectance into the equivalent absorption coefficient function, $F(R_\infty)$, where R_∞ is the ratio of the sample reflectance to the standard reflectance. The respective edge energies of the dehydrated V^{5+} molecular structures were calculated from the linear fit intercept of a plot of $(F(R_\infty)h\nu)^2$ as a function of the photon energy ($h\nu$) on the linear low-energy side of the plot (errors are usually estimated to be $\sim 0.11 \text{ eV}^{43}$). The direct band gap energy is assumed to have an absolute error lower than 0.11 eV related to the inherent uncertainty in the manual fitting process.⁴³

XAS measurements were conducted at the materials research collaborative access team bending magnet line (10-BM) of the advanced photon source, Argonne National Laboratory.⁴⁴ Measurements at the V K edge (5465 eV) were performed in the fluorescence mode using a vortex four-element detector. The sample wafer and fluorescence detector were positioned

45 and 90° relative to the X-ray beam respectively. Fluorescence-mode samples were ground into a fine powder in a mortar and pestle and pressed into a self-supporting wafer inside a stainless-steel sample holder. The potential for over-absorption artifacts was assessed by estimating the transmission edge step at the V K edge of three absorption lengths worth of sample. The calculated edge step for each sample composition was found to be well below 0.1, meaning over-absorption artifacts are negligibly small for the fluorescence data. In situ treatments were performed in a heated reaction cell described previously.⁴⁵ The sample temperature was monitored using a K-type thermocouple, and gas was introduced using a set of mass flow controllers. He, CO_2 , and 5% propane in He were acquired from airgas (ultra-high purity grade). Samples were measured as-synthesized and after a sequence of four treatments in CO_2 and $\text{C}_3\text{H}_8/\text{CO}_2$, followed by in C_3H_8 , and CO_2 after the reaction. After each treatment, the sample was cooled to room temperature in the treatment atmosphere, and spectra were collected under 100 sccm of the flowing gas. A total of six scans were collected for each treatment and averaged to yield the final data set. No discernible changes were observed between scans for a given treatment. Detailed experimental description and data analysis can be found in the [Supporting Information](#).

3. RESULTS AND DISCUSSION

3.1. Activity Performance. To evaluate the reactivity of $\text{VO}_x/\text{In}_2\text{O}_3$ catalysts, the CO_2 -ODHP reaction was conducted in the temperature range of 350–540 °C. A blank test was performed on quartz sand under the same reaction conditions, and no activity was observed ([Figure S2](#)). As shown in [Figure 1A](#), In_2O_3 shows a high C_3H_6 selectivity at a lower C_3H_8 conversion, but the selectivity decreases rapidly with the increasing conversion. All VO_x -loaded catalysts present a higher C_3H_6 selectivity than In_2O_3 under isoconversional conditions, and 3.4V/In exhibits the highest C_3H_6 selectivity among all $\text{VO}_x/\text{In}_2\text{O}_3$ catalysts. For example, at 3.3% C_3H_8 conversion, the C_3H_6 selectivity of 3.4V/In is 73%, which is ca. 1.5-fold higher than that of In_2O_3 . Moreover, 3.4V/In exhibits well-improved stability in comparison to In_2O_3 at both 500 and 540 °C within the examined time-on-stream (TOS) ([Figure 1B](#)). The reduction in C_3H_6 yield is mostly related to the decrease in conversion (deactivation) but not the decrease in selectivity. C_3H_8 conversion decreases with the addition of

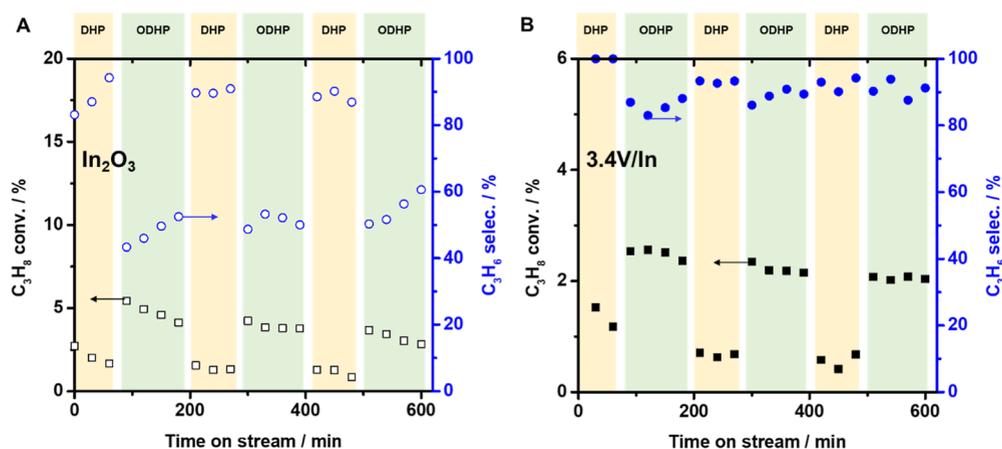


Figure 2. Catalytic performance of comparative studies between DHP and CO_2 -ODHP on In_2O_3 (A) and $3.4\text{V}/\text{In}$ (B). The reaction was conducted at 500°C . For both DHP and CO_2 -ODHP, C_3H_8 composition was fixed at 1.4%, and WHSV was $18000\text{ mL g}^{-1}\text{ h}^{-1}$. In CO_2 -ODHP, the $\text{C}_3\text{H}_8/\text{CO}_2$ ratio was 1/1.

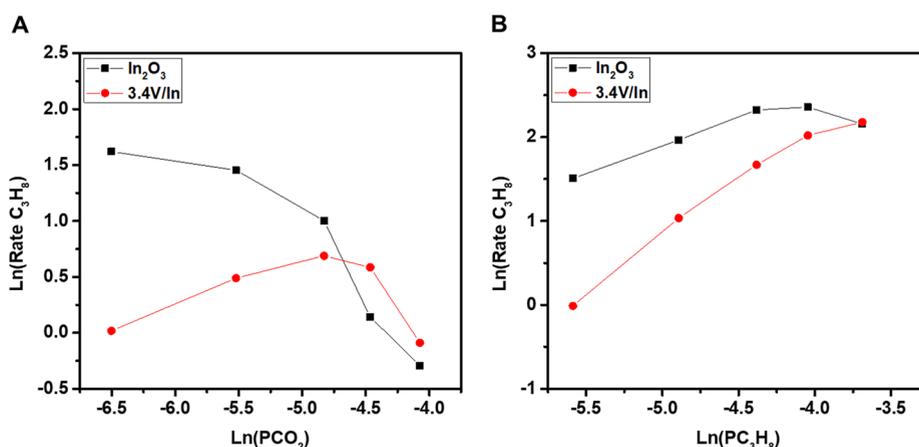


Figure 3. Effect of CO_2 (A) and C_3H_8 (B) compositions on the C_3H_8 conversion rate over $3.4\text{V}/\text{In}$ and In_2O_3 . Compositions were altered by varying the flow rates of 5% $\text{C}_3\text{H}_8/\text{He}$, 2% CO_2/Ar , and Ar with a constant total flow rate of 40 mL min^{-1} . Compositions of C_3H_8 and CO_2 were fixed at 0.8 and 1.0% for (A) and (B), respectively. All reactions were conducted at 500°C where the conversion is below 10%, and the reduction of bulk In_2O_3 is limited according to H_2 -TPR results.

VO_x , and this is even more distinct in the trend of CO_2 conversion (Figure S3).

To study the role of CO_2 in the reaction paths, comparative studies between DHP and CO_2 -ODHP were performed on $3.4\text{V}/\text{In}$ and In_2O_3 . As shown in Figure 2A, In_2O_3 presents a relatively lower C_3H_8 conversion (ca. 2%) but a higher C_3H_6 selectivity (ca. 90%) under DHP conditions. Introducing CO_2 results in a significant reduction in selectivity to ca. 50%, while the C_3H_8 conversion is almost doubled. Differently, the selectivity of $3.4\text{V}/\text{In}$ is well retained in the presence of CO_2 , together with a nearly doubled conversion (Figure 2B). The formation rate of products is also evaluated in space-time-yield (STY), as shown in Figure S4. $3.4\text{V}/\text{In}$ shows a comparable C_3H_6 STY as In_2O_3 during CO_2 -ODHP cycles and even surpasses In_2O_3 during the third cycle of CO_2 -ODHP (Figure S4A). On the other hand, the presence of CO_2 during CO_2 -ODHP significantly promotes the formation of CO on In_2O_3 in comparison to $3.4\text{V}/\text{In}$ (Figure S4B). Apparently, CO_2 plays a positive role in promoting the dehydrogenation reaction in the presence of VO_x . The CO_2 -based CO selectivity was tracked to study the carbon source of formed CO. For both RWGS and CO_2 -ODHP, the stoichiometry gives a 1/1 M ratio between consumed CO_2 and formed CO, while that ratio

is 1/2 for PDR. As shown in Figure S5, both In_2O_3 and $3.4\text{V}/\text{In}$ exhibit a CO selectivity beyond 100%, implying the contribution of PDR in CO formation other than CO_2 -ODHP. In_2O_3 presents an appreciably higher value (130–140%) than $3.4\text{V}/\text{In}$ (110–120%) under isoconversional conditions (Figure S5). In other words, 30–40% of CO originates from PDR on In_2O_3 , while that has been decreased to 10–20% from PDR on $3.4\text{V}/\text{In}$. In addition, the relationship between the $\text{CO}/\text{C}_3\text{H}_6$ molar ratio and $\text{CO}_2/\text{C}_3\text{H}_8$ conversion ratio of three cycles of CO_2 -ODHP is plotted in Figure S6. Of note, the stoichiometries of CO_2 -ODHP and PDR suggest 1/1 and 3/1 M ratios, respectively. As shown in Figure S6, the $\text{CO}_2/\text{C}_3\text{H}_8$ conversion ratio is higher than 1/1 for both In_2O_3 and $3.4\text{V}/\text{In}$, again indicating the occurrence of PDR. On the other hand, $3.4\text{V}/\text{In}$ presents a drastically lower $\text{CO}/\text{C}_3\text{H}_6$ molar ratio than In_2O_3 , clearly demonstrating a shift in reaction pathways from PDR to CO_2 -ODHP. Such a shift in reaction paths can also be reflected from mass spectrometer (MS) signals of H_2 . As shown in Figure S7, In_2O_3 shows significantly higher H_2 signals ($m/z = 2$) than $3.4\text{V}/\text{In}$ during each ODHP cycle of DHP-ODHP alternating experiments. Such a distinction also signifies the VO_x -induced shift in reaction pathways as PDR produces much more H_2 than ODHP based

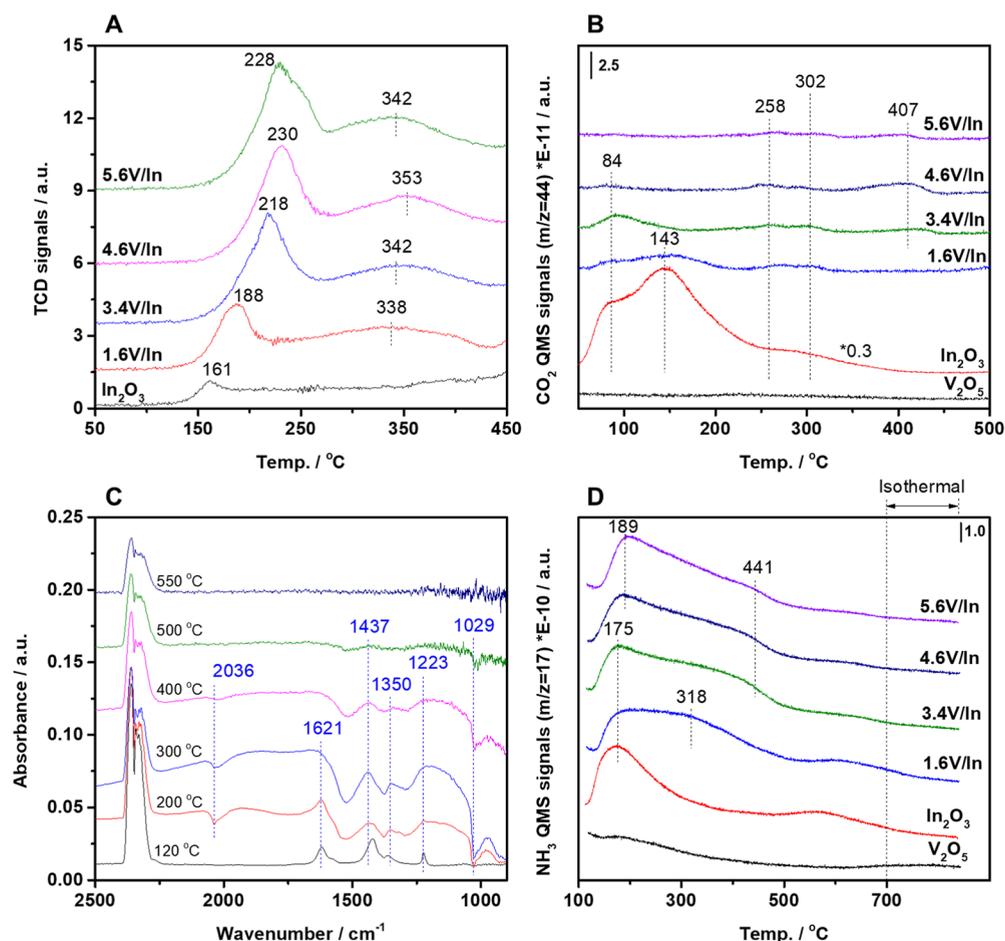


Figure 4. Reducibility and acid–base properties of $\text{VO}_x/\text{In}_2\text{O}_3$ catalysts. H_2 -TPR (A), CO_2 -TPD (B), CO_2 -DRIFTS spectra of 3.4V/In (C), and NH_3 -TPD (D) profiles for all catalysts and references.

on stoichiometry. It is further speculated that combining In_2O_3 with redox-active VO_x enables the modification of surface active sites, which leads to such a shift from PDR to CO_2 -ODHP. This will be majorly explored by characterizations, which will be discussed in the following sections.

As aforementioned, CO_2 -ODHP can proceed through two mechanisms. The first scenario includes a net reaction of DHP and RWGS, which can be linked by the H_2 produced from DHP and then consumed by RWGS.^{11,29} The other is a one-cycle mechanism, in which CO_2 closes the cycle to form CO without going through a separate RWGS step.²⁹ To provide insights into the reaction mechanisms in the presence and absence of VO_x on In_2O_3 , RWGS activity tests were performed on In_2O_3 and 3.4V/In, and the temperature-dependent H_2 and CO_2 conversions are plotted in Figure S8. Both catalysts present only RWGS activity without any detectable methanation activity. 3.4V/In shows slightly lower conversions in both reagents than In_2O_3 , especially at higher temperatures. Clearly, incorporating VO_x barely impacts the reaction pathway of RWGS but only activity. This suggests that the lower H_2 amount detected during CO_2 -ODHP over $\text{VO}_x/\text{In}_2\text{O}_3$ than In_2O_3 is not because of the extensive RWGS consumption but rather related to less H_2 production from the reactions including PDR and CO_2 -ODHP. Thus, it is reasonable to deduce that the one-cycle mechanism contributes more to CO_2 -ODHP on $\text{VO}_x/\text{In}_2\text{O}_3$.

Arrhenius plots and apparent activation energy (E_{app}) over 3.4V/In and In_2O_3 are present in Figure S9 and Table S3, respectively. Adding VO_x reduces E_{app} of C_3H_8 from 108.5 kJ mol^{-1} of In_2O_3 to 87.6 kJ mol^{-1} of 3.4V/In. This might be associated with a pathway shift from PDR to CO_2 -ODHP. Kinetics studies were then conducted on the same catalysts to examine the influence of reactant compositions on reactivity. As shown in Figure 3A, the C_3H_8 conversion rate declines monotonically with the increase in CO_2 compositions. As a more acidic molecule, CO_2 adsorption is more favorable than C_3H_8 on In_2O_3 , exerting negative impacts on propane dehydrogenation.²⁸ Differently, the conversion rate for 3.4V/In shows a volcano-like shape with the increase in CO_2 compositions. The presence of VO_x likely alleviates the competitive adsorption of reagent molecules at relatively lower CO_2 compositions (Figure 3A). This can also be associated with the VO_x -induced shift of the reaction pathway from PDR to CO_2 -ODHP. Although the competition still governs at higher CO_2 compositions, the activity of 3.4V/In starts to surpass that of In_2O_3 . As shown in Figure 3B, the competitive adsorption of reagent molecules still occurs on In_2O_3 , while that is not evident on 3.4V/In.

To evaluate coking, TPO experiments were conducted on spent catalysts by using both O_2 and CO_2 as oxidants. As shown in Figure S10A and Table S2, the peak of formed CO_2 shifts toward lower temperatures for 3.4V/In in comparison to In_2O_3 ; a reduced amount of formed CO_2 from O_2 -TPO

Table 1. Physicochemical Properties and Characterization Results of VO_x/In₂O₃ Catalysts and In₂O₃ and V₂O₅

catalyst	H ₂ consumption from H ₂ -TPR		ads. CO ₂ amt. from CO ₂ -TPD/ $\mu\text{mol g}^{-1}$	ads. NH ₃ amt. from NH ₃ -TPD/ $\mu\text{mol g}^{-1}$
	In ₂ O ₃ ^a / $\mu\text{mol g}^{-1}$	VO _x ^b / $\mu\text{mol g}^{-1}$		
In ₂ O ₃	34.5		96.6	217.5
V ₂ O ₅			0.9	14.0
1.6V/In	134.9	130.0	3.5	265.5
3.4V/In	351.4	288.7	3.1	292.0
4.6V/In	398.9	305.4	2.1	278.8
5.6V/In	426.4	379.9	1.3	262.5

^aQuantified based on the reduction peak ranging from ca. 160 to 230 °C. ^bQuantified based on the reduction peak at 340–350 °C.

profiles is observed on 3.4V/In than In₂O₃. The presence of VO_x facilitates the coke removal and resists coking. The CO₂-TPO profile confirms the formation of CO at ca. 396 °C (Figure S10B,C). The reverse Boudouard reaction likely occurs for coke removal during CO₂-ODHP.

In sum, incorporating VO_x into In₂O₃ improves the C₃H₆ selectivity and improved stability. Kinetic studies imply that VO_x plays an important role in governing the reaction pathway via propane dehydrogenation instead of PDR on In₂O₃ in the presence of CO₂. Whether these catalytic behaviors originate from the individual materials and/or in a cooperative fashion between VO_x and In₂O₃ is of interest to explore in the next step, especially their correlations with surface acid–base properties and redox cycles. For this purpose, the catalysts were characterized by various techniques, and the results will be discussed in the following sections.

3.2. Reducibility and Acid–Base Properties. **3.2.1. Reducibility.** Reducibility of catalysts was studied by H₂-TPR, and the resulting profiles are shown in Figure 4A. In₂O₃ exhibits a peak at 161 °C, corresponding to the reduction of In oxide species with smaller particle sizes.^{25,34,46,47} With the increase in V loadings, this peak gradually shifts to higher temperatures, especially from 1.6 to 3.4V nm⁻², beyond which the shift becomes less significant. Clearly, these reducible In₂O₃ species represent the ones that have intimate interactions with VO_x. A subpeak appears at 340–350 °C, which can be attributed to the reduction of VO_x species.⁴⁸ Considering the reduction peaks of bulk V₂O₅ (660–700 °C, Figure S11), these VO_x species are dispersed on In₂O₃. These reducible VO_x species increase significantly from 130.0 $\mu\text{mol g}^{-1}$ at 1.6V/In to 288.7 $\mu\text{mol g}^{-1}$ at 3.4V/In, beyond which its increase becomes slow (Table 1). A similar trend can be evidenced from the increase in the reducible In₂O₃ species ranging from 160 to 230 °C. It suggests that 3.4V nm⁻² is approaching a monolayer surface coverage, which might be associated with a higher C₃H₆ selectivity for 1.6V/In and 3.4V/In.¹ The reduction of bulk In₂O₃ starts from ca. 500 °C and presents a maximum peak at ca. 751 °C (Figure S11) for In₂O₃. Incorporating VO_x into In₂O₃ shifts the reduction of bulk In₂O₃ toward higher temperatures, indicating its role in inhibiting the deep reduction of In₂O₃ (Figure S11). Considering the lower propylene selectivity and yield and poorer stability at higher temperatures of In₂O₃ (Figure 1), it is suggested that the deep reduction of In₂O₃ has a negative impact on the catalytic performance and stability.

3.2.2. Basicity. To study the surface basicity, CO₂-TPD measurements were performed. Resultant profiles are present in Figure 4B, along with quantified CO₂ amount in Table 1. For reference materials, V₂O₅ hardly exhibits CO₂ adsorption, while In₂O₃ shows a significantly high adsorption capacity (96.6 $\mu\text{mol g}^{-1}$). On In₂O₃, the desorption peak within ca. 50–

300 °C can be attributed to adsorbed CO₂ on thermal-induced oxygen vacancies.^{36,49} CO₂-DRIFTS spectra show that CO₂ is adsorbed as carbonate and bicarbonate on In₂O₃ (Figure S12 and Table S4).^{50–52} In addition to oxygen vacancies, the surface hydroxyl groups also play a role in CO₂ adsorption, the consumption of which is evident from DRIFTS spectra (Figure S13A). The presence of VO_x considerably reduces the CO₂ adsorption capacity, especially the weakly bonded species, while retaining parts of the medium-bonded species (Figure 4B). Carbonate and bicarbonate are still evident on 3.4V/In through DRIFTS (Figure 4C and Table S5), except that the peak intensities are notably lower than those observed on In₂O₃ alone, again corroborating the suppression of CO₂ adsorption after incorporating VO_x. This is likely linked to the inhibited formation of surface oxygen vacancies and consumed hydroxyl groups by anchoring VO_x (Figure S13B). Two negative IR bands, centered at 1029 and 2036 cm⁻¹, appear on 3.4V/In (Figure 4C), which correspond to the fundamental stretching vibration and the overtone of vanadyl groups (V=O), respectively.^{53–55} The negative bands are indicative of the CO₂ adsorption on vanadyl groups.⁵⁶ In sum, adding VO_x significantly neutralizes the surface basicity of In₂O₃. Together with the retarded reduction of In₂O₃, the presence of VO_x might explain the suppressed PDR pathway.

3.2.3. Acidity. The surface acidity of the dehydrated VO_x/In₂O₃ catalysts was probed by NH₃-TPD, and the resulting profiles are shown in Figure 4D. In₂O₃ presents a major peak at ca. 175 °C with a wide range, as well as another bump at ca. 600 °C. Incorporating VO_x results in an extra peak at ca. 320–440 °C, the position of which gradually shifts to higher temperatures with the increase in V loadings. Meanwhile, the bump observed on In₂O₃ at ca. 600 °C diminishes. All VO_x/In₂O₃ catalysts exhibit a higher NH₃ adsorption capacity than In₂O₃ (Table 1). VO_x is known with its acid sites such as vanadyl groups (V=O).¹ Adding VO_x can increase the surface acid sites below or close to a monolayer-surface coverage.

The acid sites were further studied by in situ DRIFTS. In₂O₃ exhibits both Lewis (NH₃ species bands at 1622 cm⁻¹) and Brønsted bands (NH₄⁺ species at 1407 to 1434 cm⁻¹), as shown in Figure S14A. The adsorbed NH₃ on Lewis acid sites is less thermally stable than that on Brønsted acid sites as it diminishes below 300 °C. Thus, the peak at ca. 175 °C from TPD profiles (Figure 4D) signifies the NH₃ adsorption on Lewis acid sites of In₂O₃, while the bump at ca. 600 °C is indicative of the NH₃ adsorption on Brønsted acid sites such as hydroxyl groups. Both Lewis and Brønsted acid sites are also observed on 3.4V/In from Figure S14B. Except for the remaining Lewis sites on In₂O₃ responsible for the low-temperature desorption peak (~175–190 °C) from the TPD profile (Figure 4D), the VO_x-dependent peaks at ca. 320–440 °C (Figure 4D) correspond to the acid sites that are associated

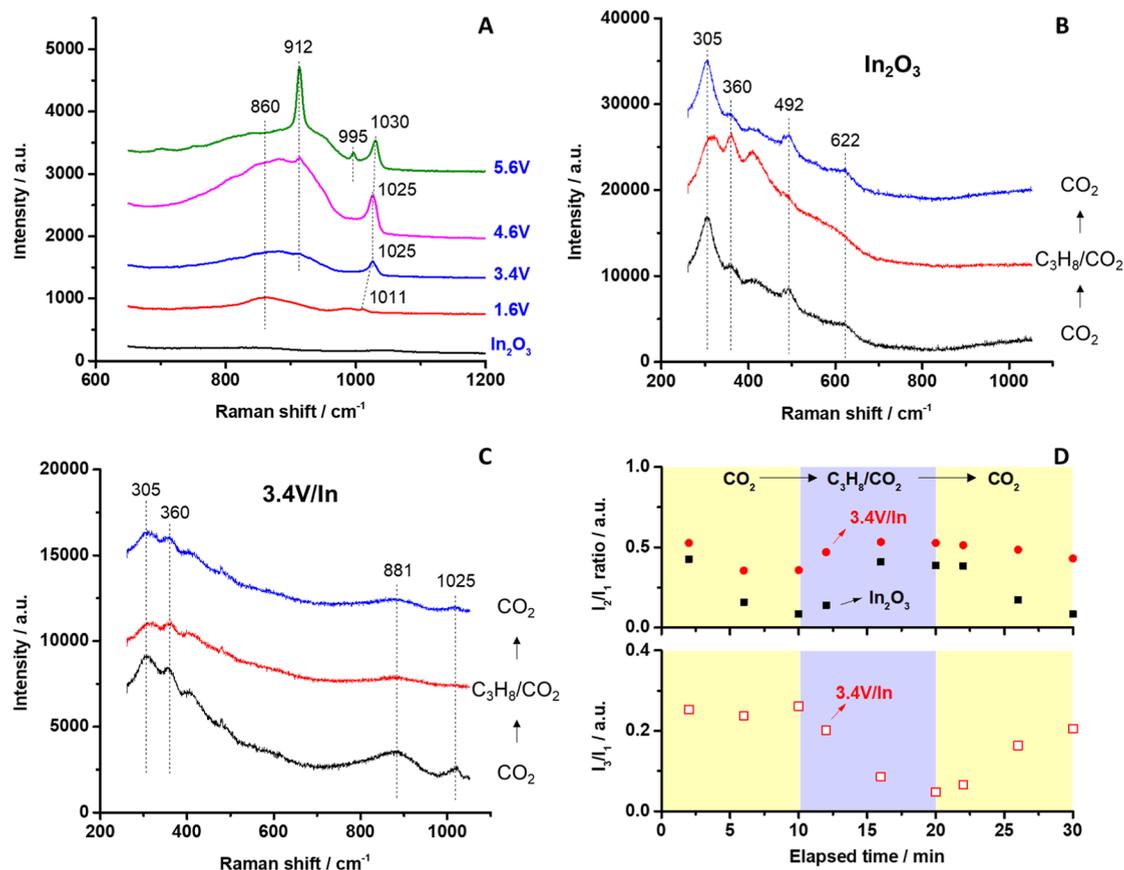


Figure 5. In situ Raman spectra of dehydrated catalysts (A), in situ Raman spectra of In_2O_3 (B) and 3.4V/In (C) under reaction conditions at 500 °C by following the sequence of $\text{CO}_2 \rightarrow \text{C}_3\text{H}_8/\text{CO}_2 \rightarrow \text{CO}_2$ with 10 min for each condition. (D) Variations in I_2/I_1 and I_3/I_1 ratios as a function of TOS under switch-mode experiments based on (B,C). I_1 : area of the peak at 305 cm^{-1} , I_2 : area of the peak at 360 cm^{-1} , and I_3 : area of the peak at 1025 cm^{-1} .

with VO_x species, such as vanadyl groups and/or bridging hydroxyl groups ($\text{V}-\text{O}(\text{H})-\text{In}$). Two negative bands, centered at 1024 and 2031 cm^{-1} , emerge upon NH_3 adsorption (Figure S14B), corresponding to the consumption of vanadyl groups of VO_x due to the interaction with NH_3 .^{1,55} The negative peak becomes less intense with the desorption temperature of NH_3 and almost disappears after 400 °C desorption, suggesting that the surface VO_x species on In_2O_3 at below or close to a monolayer coverage are responsible for the medium strength (below 400 °C in Figure 4D) acid sites.

3.3. Catalyst Structure and Redox Cycle. **3.3.1. Catalyst Structure.** Figure 5A shows the Raman spectra of all dehydrated $\text{VO}_x/\text{In}_2\text{O}_3$ catalysts at 120 °C in O_2/Ar after the pretreatment at 500 °C. For 1.6V/In, the band at 1011 cm^{-1} , corresponding to the vanadyl groups,⁵⁵ signifies the presence of less polymerized vanadates such as monovanadate. With the increase in VO_x loadings, the band gradually shifts to 1025 cm^{-1} and finally to 1030 cm^{-1} , demonstrating the progressive formation of polyvanadate on the catalyst surface. A broad peak, centered at ca. 860 cm^{-1} , emerges on all $\text{VO}_x/\text{In}_2\text{O}_3$ catalysts, indicating the presence of $\text{In}-\text{O}-\text{V}$ structure in the catalyst.^{1,55} The other V-involving species include the stretching vibration of $\text{V}=\text{O}$ for V_2O_5 particles at 995 cm^{-1} for 5.6V/In (Figure S1) and the symmetric stretching vibration of VO_4^{3-} in InVO_4 at 912 cm^{-1} for 3.4–5.6V/In catalysts.^{1,55,57–59} The Raman cross section of V_2O_5 is 10 times larger than dispersed VO_x species.⁶⁰ Based on the peak intensities in Figure 5A, dispersed VO_x is dominant. Among

these species, mono- and polyvanadates have been demonstrated as active sites for the ODHP reaction, while V_2O_5 particles lead to over-oxidation.^{1,27}

UV–vis DRS measurements were performed to verify the structure of vanadate at the surface. The Tauc plots for $\text{VO}_x/\text{In}_2\text{O}_3$ catalysts are presented in Figure S15. The edge energies of the ligand-to-metal-charge-transfer transitions of the dehydrated V^{5+} molecular structures were calculated from the abscissa intercept of the photon energy in the low-energy side of the in situ UV–vis DRS-derived Tauc plots. The increasing addition of vanadium to In_2O_3 initially results in a decrease in the edge energy from 3.13 (1.6V/In) to 2.95 eV (3.4V/In), indicating an increase in the polymerization degree of surface VO_x site. This suggests that at the lowest vanadium loading (1.6V/In), the surface VO_x species are a mix of monomeric (~20%) and polymeric (~80%) VO_4 sites.⁶¹ At higher vanadium loadings, the edge energy first decreases to 2.95 eV (3.4V/In) and then increases slightly to ~3.00 eV for both 4.6 and 5.6V/In, indicative of completely polymeric VO_4 surface sites.⁶¹ In sum, VO_x surface species polymerize progressively on In_2O_3 with loadings, with only a limited fraction of monomeric sites (~20%) present at a low surface V density of 1.6V. These observations are in general consistent with the Raman results.

In situ Raman experiments were performed to study the catalyst structures under reaction conditions. As shown in Figure 5B, In_2O_3 presents four major bands. The Raman feature at 305 cm^{-1} is interpreted as the $\delta(\text{InO}_6)$ bending

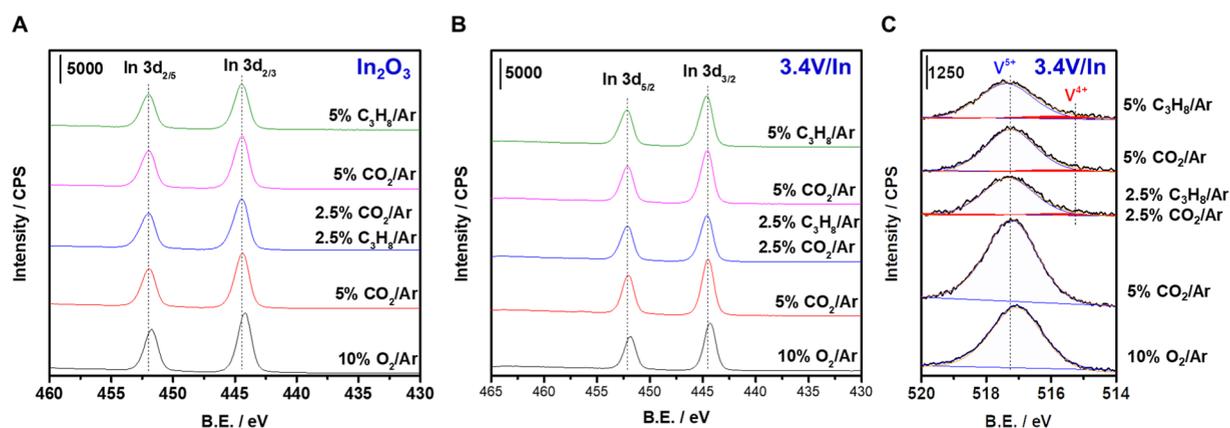


Figure 6. In situ In 3d NAP-XPS spectra of In₂O₃ (A) and 3.4V/In (B) and V 2p_{3/2} XPS spectra of 3.4V/In (C) under consecutive treatments in O₂, CO₂, C₃H₈/CO₂, and CO₂ again after the reaction for regeneration and C₃H₈ at 500 °C.

vibration of octahedra of *bcc*-In₂O₃; the band at 360 cm⁻¹ is assigned to the $\nu(\text{In-O-In})$ stretching vibration of In-O-In linkage; the other two bands at 492 and 622 cm⁻¹ correspond to the stretching vibrations of the same $\nu(\text{InO}_6)$ octahedra.^{36,49,62–64} By switching from CO₂ to C₃H₈/CO₂, the relative intensity of 360 cm⁻¹ increases and subsequently decreases after switching back to CO₂. In contrast, such a change is not significant on 3.4V/In under the same conditions (Figure 5C). The band at 360 cm⁻¹ is sensitive to the presence of oxygen vacancies in In₂O₃, and the ratio of the peak areas between 305 (*I*₁) and 360 cm⁻¹ (*I*₂) is usually adopted to quantify the relative content change in oxygen vacancies.^{63,64} As shown in Figure 5D, the ratio for In₂O₃ varies significantly by switching from CO₂ to C₃H₈/CO₂, and it appears to have more oxygen vacancies under reaction conditions than that in CO₂ alone. Recently, Hess et al. reported the oxygen and vacancy diffusion on In₂O₃ at elevated temperatures, in which the oxygen atoms diffuse to the surface for oxidation, creating oxygen defects in the bulk.⁶² Combined with this self-diffusion of oxygen, the surface of In₂O₃ alone is likely partially reduced due to the presence of the reducing agent C₃H₈, while CO₂ can reoxidize the catalyst. In contrast, the intensity ratio of 3.4V/In is relatively stable in CO₂ and C₃H₈/CO₂ (Figure 5D), signifying the role of VO_{*x*} in inhibiting the deep reduction of In₂O₃ under CO₂-ODHP reaction conditions, as well as in impeding the contact between CO₂ and surface vacancies for PDR.

DFT calculations were performed to study the effect of VO_{*x*} on the formation of vacancies on In₂O₃, and a model V₂O₅ dimer on In₂O₃ (110) was tested. As shown in Figure S16, the V₂O₅ dimer increases the oxygen vacancy formation energies to a certain extent for most lattice oxygen, such as the sites which are directly underneath VO_{*x*} (Table S6). This simple model corroborates the role of VO_{*x*} in inhibiting the deep reduction of In₂O₃. The Raman peaks of In-O-V structure and V=O in polyvanadate show an evident decrease in intensity under reaction conditions (Figure 5C). By referring the peak area of VO_{*x*} (*I*₃) to that of *I*₁ (305 cm⁻¹) (Figure 5D), quantification analysis reveals that the normalized area of VO_{*x*} decreases in the C₃H₈/CO₂ environment and recovers in the followed CO₂ treatment. This signifies a potential redox cycle of VO_{*x*} under CO₂-ODHP reaction conditions via a MvK mechanism.²⁷

3.3.2. Redox Behaviors. To gain insights into the redox characters and oxidation states, in situ NAP-XPS was

performed on 3.4V/In and In₂O₃ under conditions similar to the reaction. Figure 6A,B presents the respective In 3d XPS spectra of In₂O₃ and 3.4V/In under consecutive treatments in O₂, CO₂, C₃H₈/CO₂, and CO₂ again after the reaction at 500 °C. Based on H₂-TPR and Raman results and catalytic performance, we expected to observe different reduction behaviors of surface indium oxide species between In₂O₃ and 3.4V/In, wherein 3.4V/In should be more resistant to reduction. However, the metallic In⁰ species are absent for both catalysts and nor can be found in In MNN Auger spectra (Figure S17). A possible explanation is the diffusion of oxygen vacancies between the surface and the bulk of In₂O₃, which can maintain the surface In species under oxidized conditions.⁶² The bulk reduction via such an oxygen migration is discernible from the in situ Raman results (Figure 5). Of note, volatilization of the metallic In⁰ phase is possible at high temperatures. TGA analysis indicates that the weight loss (due to the potential volatilization of In⁰) of In₂O₃ and 3.4V/In in N₂ is limited after three-cycle measurements (Figure S18).

Figure 6C shows the XP spectra of 3.4V/In in the region of V 2p_{3/2} under similar consecutive treatments. The position of the maximal intensity barely changes, but the shape of the V 2p signal becomes less symmetric when C₃H₈ is present. This suggests the evolution of V⁴⁺ species under reaction conditions, especially in C₃H₈ alone. Besides, the normalized area of the V 2p_{3/2} region decreases after the exposure to C₃H₈ in the gas flow, implying the depletion of possibly reduced V into the bulk under reducing conditions. For the last three treatments, deconvolution analysis shows that the composition of V⁴⁺ decreases in the following order: C₃H₈ > C₃H₈/CO₂ > CO₂ (Table S7). Clearly, the joint presence of V⁴⁺ and V⁵⁺ under reaction conditions demonstrates the presence of a VO_{*x*} redox cycle under reaction conditions, in line with the Raman results. This also corroborates the contribution of VO_{*x*} to the overall activity performance via a MvK mechanism.^{1,27}

To provide more information in the redox cycle of VO_{*x*} and coordination environment of the catalysts, in situ XAS experiments were performed. Detailed data processing and analysis are elaborated in the Supporting Information (Figures S19–S25 and Tables S8–S16). Figure 7A shows the V K edge XANES spectra of 3.4V/In as synthesized and after four sequential treatments including 2.5% CO₂, 2.5% CO₂ + 2.5% C₃H₈, 2.5% C₃H₈ (post reaction), and 2.5% CO₂ (post reaction), with each treatment carried out at 500 °C for 30 min. For comparison, the XANES spectra of 3.4V/In under

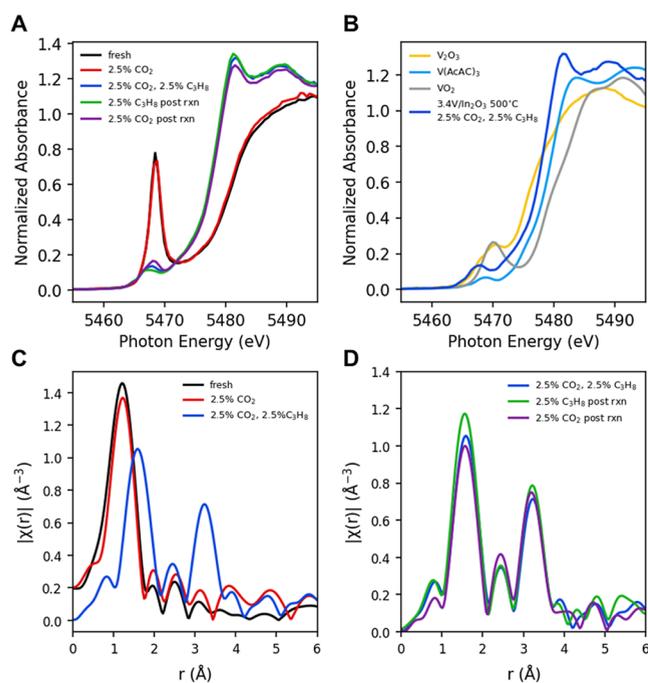


Figure 7. Vanadium K edge XANES spectra of 3.4V/In as synthesized and after in situ treatments (A), as well as the comparison between V K edge XANES spectrum of 3.4V/In after treatment in 2.5% CO₂ + 2.5% C₃H₈ (balance He) and V references V₂O₃, V(AcAc)₃, and VO₂ (B). (C) R space V K edge EXAFS spectra of fresh 3.4V/In and the same catalyst after sequential treatment in 2.5% CO₂ and 2.5% CO₂ + 2.5% C₃H₈, as well as those after sequential treatments in 2.5% C₃H₈ and 2.5% CO₂ after the reaction in 2.5% CO₂ + 2.5% C₃H₈ (D). Treatment conditions are detailed in Table S8.

C₃H₈/CO₂ is plotted with reference materials V₂O₃, VO₂, and V(AcAc)₃ in Figure 7B. The pre-edge peak of 3.4V/In after the treatment in C₃H₈/CO₂ is at a lower energy than V(AcAc)₃ and an intensity intermediate between V₂O₃ and V(AcAc)₃, implying that vanadium has a local environment distinct from the octahedral or distorted octahedral symmetry of V(AcAc)₃ or V₂O₃. The edge position that lies between the two V³⁺ references suggests that V is in the 3+ oxidation state. This is consistent with the XPS results, in which V³⁺ is missing from the surface region, and some of the V is depleted from the surface region under C₃H₈. The XANES of samples treated post reaction sequentially in C₃H₈-post and then in CO₂-post show subtle variation in pre-edge shape and edge energy compared to the one treated in C₃H₈/CO₂ (Figure 7A). This could be caused by partial redox or due to adsorbates on surface vanadium sites.

Figure 7C,D shows the V K edge R space EXAFS of 3.4V/In after the same sequential treatments, along with the structural parameters in Table 2. The fresh and CO₂-treated catalysts have similar spectra, with a single large peak centered at 1.2 Å (phase uncorrected distance) due to V–O scattering. After the treatment in CO₂, V–O coordination number drops to 4.2, which is likely due to the dehydration. The short V–O bond distance (1.65 Å) and V–O coordination number (4–5) are consistent with V in the 5+ oxidation state. No distinct structure is observed past the first shell which reflects the configurational complexity of surface vanadium sites. In contrast, after the treatment in C₃H₈/CO₂, strong second and third shell scatterings are seen. This implies a more crystalline local structure around vanadium after treatment. To model the structure after C₃H₈/CO₂ treatment, it was necessary to include both a V–O bond and a V–C bond to properly fit the first shell. The extended structure was modeled using V–V and V–In scattering paths within an In–V mixed oxide. The long V–O bond distance (2.066 Å) is consistent with a more reduced vanadium and in agreement with the reduced edge energy seen in the XANES. The appearance of a more ordered V environment after C₃H₈/CO₂ treatment may explain the difference in the oxidation state seen in XAS versus by XPS measurement. While XPS only measures V species in the near surface region, XAS measures all V present in the sample. The reduction to V³⁺ may allow vanadium to diffuse into the In₂O₃ lattice rapidly, which would explain the intensity loss in XPS after reducing treatment and the appearance of an ordered V environment in XAS.

After the treatment in the C₃H₈-post reaction (Figure 7D), the V–O coordination number remains unchanged, while the V–V and V–In coordination numbers drop by 0.6 and 0.9, respectively. The V–C coordination number increases from 0.3 to 0.5. A subsequent treatment in CO₂-post reaction increases the V–M (V or In) coordination numbers close to the values seen after the C₃H₈/CO₂ treatment. In the first shell, the CO₂ post reaction treatment causes the V–O coordination number to change from 3.5 to 2.9. Additionally, all V–C coordination is lost, and instead a short V–O bond is observed at 1.591 Å, indicative of the oxidation of V to higher oxidation states.

Taken together, these changes in coordination numbers show that under reaction conditions (C₃H₈/CO₂), vanadium reduces and forms a mixed oxide with In₂O₃. A fraction of surface vanadium sites has bonded with a carbon-containing species, likely derived from propane under conditions of both C₃H₈/CO₂ and C₃H₈ alone. When treated in C₃H₈ alone, this surface coverage of carbon-containing species increases, and the V–M coordination number decreases. Likely, the reduction, occurring in the subsurface, results in the loss of

Table 2. Structural Parameters of V–O and V–M Coordination Shells for 3.4V/In Catalysts Treated under Different Conditions

treatment	V–O		V–(C/O) ^a		V–V		V–In	
	CN	R (Å)	CN	R (Å)	CN	R (Å)	CN	R (Å)
Fresh	5.3 ± 1.6	1.67 ± 0.02						
CO ₂	4.2 ± 1.3	1.69 ± 0.02						
C ₃ H ₈ /CO ₂	3.5 ± 0.4	2.066 ± 0.006	0.3 ± 0.2	1.672 ± 0.006	1.4 ± 0.6	3.265 ± 0.009	6.0 ± 1.0	3.365 ± 0.009
C ₃ H ₈ -post	3.5 ± 0.4	2.063 ± 0.006	0.5 ± 0.2	1.629 ± 0.005	0.8 ± 0.5	3.262 ± 0.009	5.1 ± 0.9	3.363 ± 0.009
CO ₂ -post	2.9 ± 0.3	2.057 ± 0.005	0.2 ± 0.1	1.591 ± 0.005	1.3 ± 0.5	3.252 ± 0.008	5.5 ± 0.8	3.353 ± 0.008

^aThe second light scatterer in the first shell is V–C for C₃H₈/CO₂ and C₃H₈-post and is V–O for CO₂-post.

oxygen and breaking of In–O–V (as evidenced by a smaller V–O coordination number), followed by the self-diffusion of bulk oxygen to oxidize the surface.⁶² This agrees with the observations from Raman results, in which the reduction and reoxidation of In₂O₃ are evidenced in the presence of C₃H₈ and CO₂, respectively (Figure 5). Treating in CO₂ removes the carbon-containing species bonded to V and regenerates the V–O bond. These results are consistent with vanadium sites acting as binding sites for propane adsorption and dehydrogenation and with CO₂ acting as a soft oxidant facilitating its removal.

4. DISCUSSION

Raman and UV–vis DRS results reveal the presence of the In–O–V structure and dispersed polyvanadates for 3.4V/In with the optimal composition for the CO₂-ODHP performance. In situ Raman, NAP-XPS, and XAS spectra provide strong evidence of the redox cycle of VO_x under reaction conditions, wherein CO₂ plays a role in reoxidizing V³⁺/V⁴⁺ to V⁵⁺. It is critical to link these observations with the acid–base and redox properties of VO_x/In₂O₃ catalysts, as well as to advance the understanding of their correlations with the well-retained high C₃H₆ selectivity and improved stability.

In₂O₃ is a known catalyst candidate for ODHP reactions; however, its reaction mechanism is elusive.^{11,33} Our in situ Raman results demonstrate the reduction and reoxidation of In₂O₃ under C₃H₈/CO₂ and CO₂ conditions, respectively (Figure 5). Although Raman probes the bulk, the redox has to start from the surface and then dynamically propagates into the bulk. Besides, the identified reducible In₂O₃ species that have intimate interactions with VO_x species from H₂-TPR profiles (160–230 °C from Figure 4A) are likely those redox-active InO_x species. Thus, the redox property of InO_x might play a role in CO₂-ODHP, similar to MvK on VO_x.¹ However, in situ NAP-XPS and AES results present a stable oxidation state of In species on the surface (Figure 6). Likely, the redox cycle happens too fast to be captured, or volatilization of metallic In may occur, both of which are responsible for the missing metallic In phase from spectra. As a result, even if the redox cycle of InO_x indeed presents, it is limited based on our observations. In other words, both heterolytic dissociation and MvK are possible for In₂O₃ for CO₂-ODHP. This is the place where more effort is needed in the future.

Our NAP-XPS results indicate that the surface In species stay at a stable oxidation state in the case for In₂O₃ during reactions (Figure 6). Thus, a similar heterolytic dissociation mechanism might be applicable to In₂O₃. Based on H₂-TPR and Raman results, a deep reduction of In₂O₃ occurs at higher temperatures (>500 °C, Figures 4 and S11), which results in decreased selectivity and deactivation. The first crucial role of surface vanadates and the bridging In–O–V structure is to help resist the deep reduction of In₂O₃ under reaction conditions, therefore maintaining the selectivity and improving the stability for CO₂-ODHP.

In₂O₃ is a basic metal oxide that features CO₂ adsorption on oxygen vacancies.^{35,49,63,65,66} However, such a strong affinity toward CO₂ may “poison” the surface to favor CO₂ adsorption and activation for side reactions such as PDR. Most recently, by studying a series of Pd bimetallic catalysts for CO₂-assisted ethane dehydrogenation, Chen et al. showed that a metallic surface favors dry reforming, while an oxidic surface favors C–H scission in ethane.⁶⁷ Linked to our observations, it is suggested that the reduction of In₂O₃ under reaction

conditions is another reason resulting in PDR and impairing the C₃H₈ dehydrogenation on In₂O₃. The presence of vanadates neutralizes these basic sites and inhibits the deep reduction of In₂O₃, as evidenced by the chemisorption results (Figure 4 and Table 1). This further enables the suppression of PDR, resulting in an enhanced C₃H₆ selectivity.

Studies of reaction paths in the current work shows that CO₂-ODHP proceeds more through a one-cycle mechanism. In specific, CO₂ can form CO without undergoing a separate RWGS step. In this case, CO₂ plays a role in reoxidizing the VO_x and potentially InO_x to close the redox cycles, releasing CO and H₂O as products. Noteworthily, the produced amount of CO is much less in CO₂-ODHP than that in PDR, which can be reflected from the retained higher C₃H₆ selectivity over V/In catalysts than that over In₂O₃. Therefore, the second role of VO_x is to shift the role of CO₂ from contributing to PDR on In₂O₃ to completing the redox cycle for propane dehydrogenation as a soft oxidant. This is a promising way of utilizing the reagent molecules for a desired reaction pathway.

5. CONCLUSIONS

In this work, we prepared a series of VO_x/In₂O₃ with various surface V densities and compared the activity performance with In₂O₃ alone for CO₂-ODHP. On In₂O₃, the C₃H₆ selectivity decreases sharply with the increase in C₃H₈ conversion and drops below 50% beyond 4% C₃H₈ conversion, as well as poor stability. This can be ascribed to the strong basicity and reduced In₂O₃ during ODHP that favor PDR to CO when the deep reduction occurs, especially at higher temperatures. In contrast, all VO_x-loaded catalysts not only present higher C₃H₆ selectivity than In₂O₃ under isoconversional conditions (higher than 60% at 4% C₃H₈ conversion), but they also exhibit improved stability. The optimal surface V density is obtained at 3.4V nm⁻² for CO₂-ODHP. Detailed characterization results identify the bridging In–O–V structure and dispersed mono-/polyvanadate on In₂O₃ at the VO_x loading below a monolayer coverage (between 3.4 and 4.6V/nm²). The presence of the In–O–V structure and dispersed VO_x species can help resist In₂O₃ reduction and suppress PDR, resulting in better selectivity and stability. Also, VO_x itself contributes to the overall catalytic performance through the redox cycle by using CO₂ as a soft oxidant. These findings provide insights into designing selective, robust catalysts for the CO₂-ODHP reaction by manipulating the interplays between the redox property and acid–base interaction in catalysts based on mixed oxides.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.2c02099>.

Detailed ICP results; additional results of activity tests, kinetic studies, and MS results; activity data of RWGS; coke analysis via O₂-TPO; H₂-TPR profiles, NH₃-DRIFTS, and CO₂-DRIFTS spectra; in situ Raman spectra collected under pretreatment and reaction conditions; DFT methods and model structures; in situ NAP-XPS spectra and quantification results; TGA profiles after cycles; and in situ XAS spectra and data analysis (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported as part of the Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE ME), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences at the under award #

DE-SC0012577. Part of the work including the synthesis, activity test, DFT calculations, and characterizations (chemisorption, DRIFTS, and in situ Raman Spectroscopy) was carried out at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. MRCAT operations are supported by the Department of Energy and the MRCAT member institutions. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract no. DE-AC02-06CH11357. In situ NAP-XPS and Part of the in situ Raman spectroscopy were performed at the Operando Molecular Spectroscopy and Catalysis Research Laboratory of Lehigh University.

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