Interaction between V$_2$O$_5$ nanowires and high pressure CO$_2$ gas up to 45 bar: Electrical and structural study

Hyun-Seok Jang$^{a,b,c,1}$, Chang Yeon Lee$^{d,1}$, Jun Woo Jeon$^{a,b,c}$, Won Taek Jung$^{a,b,c}$, Junyoung Mun$^d$, Byung Hoon Kim$^{a,b,c,*}$

$^a$Department of Physics, Incheon National University, 22012 Incheon, Republic of Korea
$^b$Institute of Basic Science, Incheon National University, 22012 Incheon, Republic of Korea
$^c$Intelligent Sensor Convergence Research Center, Incheon National University, 22012, Incheon, Republic of Korea
$^d$Department of Energy and Chemical Engineering, Incheon National University, Incheon 22012, Republic of Korea

highlights

- CO$_2$ gas pressure-dependent conductance ($G(P)$) of vanadium-oxides nanowires (VON) from vacuum to 45 bar decreases with the increase of the gas pressure.
- Increase in the interlayer distance and decrease in phonons for V=O and V-O-V bonds were observed after high CO$_2$ pressure exposure.
- Oxidation of V$^{4+}$ to V$^{5+}$ due to high CO$_2$ pressure is the reason for these changes.
- Oxidative dehydrogenation process with VON catalyst under high pressure CO$_2$ atmosphere has potential to improve the efficiency.

abstract

In the oxidative dehydrogenation (ODH) process that converts ethylbenzene to styrene, vanadium-based catalysts, especially V$_2$O$_5$, are used in a CO$_2$ atmosphere to enhance process efficiency. Here we demonstrate that the activation energy of V$_2$O$_5$ can be manipulated by exposure to high pressure CO$_2$, using V$_2$O$_5$ nanowires (VON). The oxidation of V$^{4+}$ to V$^{5+}$ was observed by X-ray photoelectron spectroscopy. The ratio of V$^{4+}$/V$^{5+}$ which the typical comparable feature decreased 73.42%. We also found an increase in the interlayer distance in VON from 9.95 Å to 10.10 Å using X-ray diffraction patterns. We observed changes in the peaks of the stretching mode of bridging triply coordinated oxygen (V=O), and the bending vibration of the bridging V-O-V, using Raman spectroscopy. We confirmed this propensity by measuring the CO$_2$ pressure-dependent conductance of VON, up to 45 bar. 92.52% of decrease in the maximum conductance compared with that of the pristine VON was observed. The results of this study suggest that ODH process performance can be improved using the VON catalyst in a high pressure CO$_2$ atmosphere.

© 2020 THE AUTHORS. Published by Elsevier BV on behalf of Cairo University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Introduction

Carbon is the most fundamental element in ecological systems and biological organisms. The atmospheric concentration of carbon gas, particularly carbon dioxide ($\text{CO}_2$), is also known to be the one of the main factors driving climate change, global warming and ocean acidification. Nevertheless, $\text{CO}_2$ gas is widely used in industry, especially for styrene production.

Styrene is a mainstay material in the polymer industry. It is mostly produced using ethylbenzene via the oxidative dehydrogenation (ODH) process with a transition metal oxide [1–7]. Under the presence of inorganic oxidants, such as metal oxides reported in the last decades, the ODH process of organic aromatic compounds is accelerated [8–11]. Among various metal oxides, vanadium-based catalysts with various support materials have been focused because of their good catalytic performance, particularly styrene yields and selectivity [12–20]. In ODH using a vanadium-based catalyst, especially $\text{V}_2\text{O}_5$, the valence state of the vanadium switches back and forth between $\text{V}^{4+}$ and $\text{V}^{5+}$ as shown in Fig. 1 [21,22]. However, the persistent reduction of $\text{V}^{5+}$ to $\text{V}^{4+}$ results in catalyst deactivation. In other words, a large amount of $\text{V}^{5+}$ compared with that of $\text{V}^{4+}$ enhances the activation process.

A large amount of superheated steam has generally been used in the process as an oxidant, but in recent years, $\text{CO}_2$ gas has become the preferred alternative oxidant, due to its advantages [1–7,12–20]. For example, in a $\text{CO}_2$ atmosphere the latent heat is maintained throughout the entire reaction process [23] and there is a greater decrease in the partial pressure of the reactants with $\text{CO}_2$ than with superheated steam [24]. This is the reason for the growing industrial interest in $\text{CO}_2$ gas mentioned above.

It has been reported that high gas pressure can lower the dissociation energy of the gas, resulting in the modulation of the physical and electronic properties of 2D materials [25–30]. This suggests that high gas pressure can enhance the catalytic effect. Moreover, if small sized $\text{V}_2\text{O}_5$ is used as a catalyst, it is expected that the ODH reaction will be reinforced because of the increase in surface area.

In this study, we synthesized $\text{V}_2\text{O}_5$ nanowires (VON) and investigated their structural modulation and electrical transport property as a function of $\text{CO}_2$ gas pressure from vacuum to 45 bar. The pressure-dependent Transconductance ($G(P)$) decreased as the pressure increased, due to oxidation of the VON. This behavior was clarified by x-ray photoelectron spectroscopy (XPS), and structural changes were studied by x-ray diffraction (XRD) pattern and Raman spectroscopy before and after exposure to high pressure $\text{CO}_2$. We found an increase in the $\text{V}^{5+}$ state, after the VON were exposed to high $\text{CO}_2$ pressure. From the results in this study, we suggest that an ODH process with a VON catalyst can be improved by high-pressure $\text{CO}_2$ atmosphere.

Experimental

Synthesis of the $\text{V}_2\text{O}_5$ nanowires

The VON was synthesized using a sol-gel method involving the polycondensation of vanadic acid in water [31]. VONs were synthesized from 5 g ammonium meta-vanadate (Aldrich) and 50 g acidic ion-exchange resin (DOWEX 50WX-100, Aldrich) in 1 L deionized water, and then the mixture was kept at room temperature to produce an orange sol that darkened with time.

Measurement electrical transport property of VON with respect to $\text{CO}_2$ gas pressure

Sol-gel based VON film was synthesized with VON by drying at 80 °C for 48 h in an atmospheric condition. The dried VON film was cut into 1 × 5 mm sections, and attached to an insulating substrate to measure its electrical conductance as a function of $\text{CO}_2$ gas pressure using a home-made pressure chamber.

The VON film in the pressure chamber was heated at 80 °C and high vacuum condition ($1 \times 10^{-6}$ Torr) for 3 h to remove residues. After annealing, the VON film was cooled down to 300 K (300.00 K ± 0.20 K) and the temperature was maintained during the entire measurement process.

In this study, 99.999% $\text{CO}_2$ gas was used. $\text{CO}_2$ pressure was increased by 5 bar up to 45 bar. $G(P)$ was measured 30 min after reaching each target pressure. $G(P)$ was fitted from the $I$-$V$ curve of the VON film (the applied voltage was from −200 mV to 200 mV, in 2 mV steps using a KEITHLEY SCS-4200, U.S.A.).

Characterization of VON and $\text{CO}_2$-VON

The morphology of the VON was observed using a scanning electron microscope (SEM, JEOL, JSM-7800F, Japan). The chemical species and structure of the VON and $\text{CO}_2$-VON were investigated by Raman spectroscopy (Witec, Alpha-300, Germany), X-ray photoelectron spectroscopy (XPS, ULVAC, PHI-5000 VersaProbe II, Japan), and X-ray diffraction (XRD, Rigaku, SmartLab HR-XRD, Japan).

![Fig. 1. Schematic for the mechanism of the ODH process of ethylbenzene with and without the presence of $\text{V}_2\text{O}_5$ as a catalyst.](image-url)
Results and discussion

Morphology and structural investigation with SEM, XRD, and Raman spectroscopy

Fig. 2(a) shows the SEM image of the VON. VON with diameters of about 10–20 nm, which is well consistent with the previous literatures [31–33]. The normalized XRD patterns of pristine VON and VON after high-pressure CO2 gas exposure (CO2-VON) are shown in Fig. 2(b). The (0 0 1) peak of the CO2-VON has shifted to a smaller angle (2θ = 8.88 for VON and to 8.75° for CO2-VON, the inset of Fig. 2(b)), which indicates that the interlayer distance of the VON increased from 9.95 to 10.10 Å after CO2 exposure. In order to confirm the structural modulation, Raman spectroscopy was performed.

Fig. 2(c) shows the normalized Raman peaks. The characteristic VON peaks were found [34–36]. The dominant peaks at 139 and 193 cm⁻¹ originate from the relative motions of two V₂O₅ units belonging to the unit cell. The peaks at 280 and 405 cm⁻¹ are associated with the bending vibration of the V=O bond. The peaks at 689 and 991 cm⁻¹, respectively, correspond to the bending vibration of doubly coordinated oxygen (V₂–O) and the stretching vibration mode of the shortest V–O₁. These six peaks did not change even after high CO₂ pressure exposure. The peaks at 297, 522, and 476 cm⁻¹ were assigned to the bending vibration, the stretching mode of the bridging triply coordinated oxygen (V₁–O), and the bending vibration of the bridging V–O–V, respectively. Although the peak intensity changed little, these three peaks were reduced after VON exposure to high CO₂ gas pressure (see Fig. S1 in Supplementary Information and the inset in Fig. 2(c)).

This can be interpreted as follows. The amount of V₂O₅ and V₁–O bonds in the VON after CO₂ exposure increased from 37.07 to 54.61%. V₂O₃, V₂O₅ (V⁵⁺), and VO₂ (V⁴⁺) species were observed in V 2p³/₂. Note that the amount of V₂O₅ species significantly increased from 48.05%.

Electrical transport property of VON with respect to CO₂ gas pressure

Fig. 3 shows the electrical transport property of VON as a function of CO₂ gas pressure from vacuum (~10⁻⁶ Torr) to 45 bar. As soon as the VON was exposed to 5 bar of CO₂ gas, the G(P) of the VON dramatically decreased from 26.33 to 13.92 μA, and then it gradually declined down to 1.97 μA at 45 bar of CO₂ pressure. This behavior is similar to the oxygen pressure-dependent conductance of VON [37].

In general, charge transport in VON has been interpreted to be by small polaron hopping. The concentration ratio of V⁴⁺/(V⁴⁺ + V⁵⁺) plays an important role in this transport behavior [25]. Specifically, the amount of V⁴⁺ and V⁵⁺ significantly affects the charge transport property, which is related to oxygen vacancies. It is well known that the charge carrier density in VON is proportional to the density of oxygen vacancies. Oxygen vacancies cause the reduction of V⁵⁺, producing V⁴⁺, which can be understood as V⁵⁺ plus an additional electron [38]. This means that the electrical conductance of VON decreases when oxygen vacancies are reduced.

X-ray photoelectron study before and after CO₂ exposure

For this reason, the valence state of the vanadium in VON before and after exposure to CO₂ was studied using XPS (Fig. 4). The surveys of pristine VON and CO₂-VON are depicted in Fig. S2 in the Supplementary Information. Vanadium, oxygen, and carbon species were observed. The carbon peak in the pristine originates from the carbon tape used to support the sample, so we did not consider this peak. The peaks at approximately 530, 524, and 517 eV correspond to O 1s, V 2p₁/₂, and V 2p₃/₂ (Fig. 4). The O 1s peak consisted of three sub-peaks: V=O at 533.29 eV, V–O–V at 531.65 eV, and O²⁻ at 530.29 eV. The amount of V–OH slightly increased after CO₂ exposure (Table 1). This shows that the surface OH rarely changes after annealing and CO₂ exposure.

On the other hand, the amount of V–O–V bonds in the VON after CO₂ exposure increased from 37.07 to 54.61%. V₂O₃, V₂O₅ (V⁵⁺), and VO₂ (V⁴⁺) species were observed in V 2p₃/₂. Note that the amount of V₂O₃ species significantly increased from 48.05%.
for VON, to 71.89% for CO2-VON, but the VO2 species decreased from 45.72% to 18.18%.

Since the charge transport in VON is mainly governed by the amount of V4+ and V5+ as mentioned above, we focused on the vanadium species. The ratio of V4+/V5+ changed from 0.952 for the pristine VON to 0.253 for CO2-VON. The decrease in V4+/V5+ in the VON after CO2 exposure indicates that the VON was oxidized due to CO2. A notable point is that \( G(P) \) continuously decreased and saturated with the increase in CO2 pressure. This means that the high CO2 pressure enhanced the oxidation of the reduced VON.

Conclusions

This study investigated the effect of high CO2 gas pressure on VON conductivity, and revealed that pressure-dependent oxidation intrinsically reduced the VON. \( G(P) \) continuously decreased as CO2 pressure increased, which resulted in an increase in V5+. This behavior was confirmed by XPS taken before and after exposure to high CO2 pressure. Upon CO2 gas exposure, the ratio of V4+/V5+ was reduced by four times. Structural modulation resulting from CO2 gas exposure was also studied by XRD and Raman spectroscopy. The interlayer distance in the VON increased from 9.95 to 10.10 Å, due to an increase in the amount of V-O-V and V-O bonds. This study provides a potential method for improving the ODH process using a VON catalyst in a high-pressure CO2 atmosphere.

Ethics statement

This article does not contain any studies with human or animal subjects.

Acknowledgement

This work was supported by the Incheon National University Research Grant in 2016-2328 and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2017R1A1A05000789).

Declaration of Competing Interest

The authors declare no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jare.2020.01.014.

References

[1] Li X, Feng J, Fan H, Wang Q, Li W. The dehydrogenation of ethylbenzene with CO2 over Ce2Zr1-xOx solid Solutions. Catal. Commun. 2015;59:104-7.
[2] Burri A, Jiang N, Yahyaoui K, Park S-E. Ethylbenzene to styrene over alkali doped TiO2-ZrO2 with CO2 as soft oxidant. Appl. Catal. A: Gen. 2015;495:192–9.
[3] Wang T, Guan X, Lu H, Liu Z, Ji M. Nanoflake-assembled Al2O3-supported CeO2-ZrO2 as an efficient catalyst for oxidative dehydrogenation of ethylbenzene with CO2. Appl. Surf. Sci. 2017;398:1–8.
[4] Wang C, Shi J, Cui X, Zhang J, Zhang C, Wang L, et al. The role of CO2 in dehydrogenation of ethylbenzene over pure α-Fe2O3 catalysts with different facets. J. Catal. 2017;345:104–12.
[5] Wang T, Qi L, Lu H, Ji Min. Flower-like Al2O3-supported iron oxides as an efficient catalyst for oxidative dehydrogenation of ethylbenzene with CO2. J. CO2 Util. 2017;17:162–9.
[6] Wang T, Chong S, Wang T, Lu H, Min J. The physicochemical properties and catalytic performance of carbon-covered alumina for oxidative dehydrogenation of ethylbenzene with CO2. Appl. Surf. Sci. 2018;427:1011–8.

[7] Wang H, Yang G-Q, Song Y-H, Liu Z-T, Liu Z-W. Defect-rich CeO2–ZrO2 solid solutions for oxidative dehydrogenation of ethylbenzene with CO2. Catal. Today 2019;324:39–48.

[8] Li XG, Liao Y, Huang MR, Strong Y, Kaner RB. Ultra-sensitive chemosensors for Fe (II) and explosives based on highly fluorescent oleofluoranthenes. Chem. Sci. 2013;4(5):1970–8.

[9] Li XG, Liao Y, Huang MR, Kaner RB. Efficient synthesis of oleofluoranthenic nanorods with tunable functionalities. Chem. Sci. 2015;6(12):7190–200.

[10] Li XG, Liu YW, Huang MR, Peng S, Gong LZ, Moloney MG. Simple efficient synthesis of strongly luminescent polypyrrole with intrinsic conductivity and high carbon yield by chemical oxidative polymerization of pyrrole. Chem.–A Eur. J. 2010;16(16):4803–13.

[11] Sakurai Y, Suzuki T, Benaga N-O, Suzuki T. Dehydrogenation of ethylbenzene with an activated carbon-supported vanadium catalyst. Appl. Catal. A: Gen. 2000;192:281–8.

[12] Liu BS, Chang RZ, Jiang L, Liu W, Au CT. Preparation and high performance of La2O3–V2O5/MCM-41 catalysts for ethylene oxide dehydrogenation in the presence of CO2. J. Phys. Chem. C. 2008;112:15490–501.

[13] Rao KN, Reddy BM, Abhishek B, Seo Y-H, Jiang N, Park S-E. Effect of ceria on the structure and catalytic activity of V2O5/TiO2–ZrO2 for oxodehydrogenation of ethylbenzene to styrene utilizing CO2 as soft oxidant. Appl. Catal. B: Environ. 2009;91:649–56.

[14] Wang C, Fan W-B, Liu Zi-T, Liu J, Liu Z-W, Qin Z-F, et al. The dehydrogenation of ethylbenzene with CO2 over V2O5/Co3O4–ZrO2 prepared with different methods. J. Mol. Catal. A: Chem. 2010;329:64–70.

[15] Liu Z-W, Wang C, Fan W-B, Liu Z-T, Hao Q-Q, Long X, et al. V2O5/CeO2/ZrO2–Al2O3 as an efficient catalyst for the oxidative dehydrogenation of ethylbenzene with carbon dioxide. Chem. Sus. Chem. 2011;4:341–5.

[16] Chen S, Qin Z, Wang G, Dong M, Wang J. Promoting effect of carbon dioxide on the dehydrogenation of ethylbenzene over silica-supported vanadium catalysts. Fuel 2013;109:43–8.

[17] Zhang S, Li X, Jing J, Fan H, Wang Q, Li W. Dehydrogenation of ethylbenzene with CO2 over V2O5/Al2O3–ZrO2 catalyst. Catal. Commun. 2013;34:5–10.

[18] Fan H, Feng J, Li X, Guo Y, Li W, Xie K. Ethylbenzene dehydrogenation to styrene with CO2 over V2O5 (001): a periodic density functional theory study. Chem. Eng. Sci. 2015;135:403–11.

[19] Betiha MA, Rabie AM, Ellady AM, Yehia FZ. Microwave assisted synthesis of a VOx–modified disordered mesoporous silica for ethylbenzene dehydrogenation in presence of CO2. Micropor. Mesopor. Mater. 2016;222:44–54.

[20] Kainthla I, Babu GVR, Bhanushali JT, Keri RS, Rao KSR, Nagaraja BM. Vapor-phase dehydrogenation of ethylbenzene to styrene over a V2O5/Al2O3–ZrO2 catalyst with CO2. New J. Chem. 2017;41(10):4173–81.

[21] Zhao X, Yan Y, Mao L, Fu M, Zhao H, Sun L, et al. A relationship between the V+/V0 ratio and the surface dispersion, surface acidity, and redox performance of V2O5–WO3/TiO2 SCR catalysts. RSC Adv. 2018;8(54):31081–93.

[22] Adams CR, Jennings TJ. Catalytic oxidations with sulfur dioxide: II. Alkylation reactions. J. Catal. 1970;17:157–77.

[23] Chen S, Qin Z, Xu X, Wang J. Structure and properties of the alumina-supported vanadia catalysts for ethylbenzene dehydrogenation in the presence of carbon dioxide. Appl. Catal. A: Gen. 2006;302:185–92.

[24] Kim BH, Hong SJ, Baek SJ, Jeong HY, Park N, Lee M, et al. N-type graphene induced by dissociative H2 adsorption at room temperature. Sci. Rep. 2012;2:690.

[25] Hong SJ, Park M, Kang H, Lee M, Soler-Delgado D, Shin DS, et al. Verification of electron doping in single-layer graphene due to H2 exposure with thermoelectric power. Appl. Phys. Lett. 2015;106:142110.

[26] Kim J, Kwak CH, Jung W, Huh YS, Kim BH. Variation in the c-axis conductivity of multi-layer graphene due to H2 exposure. Phys. Chem. Chem. Phys. 2016;18:15514–8.

[27] Hong SJ, Park M, Kang H, Lee M, Soler-Delgado D, Jeong DH, et al. Manipulation of electrical properties in CVD-grown twisted bilayer graphene induced by dissociative hydrogen adsorption.Curr. Appl. Phys. 2016;16:1637–41.

[28] Hong SJ, Kim H, Lee M, Kang H, Park M, Jeong DH, et al. Chemical manipulation of edge-contact and encapsulated graphene by dissociated hydrogen adsorption. RSC Adv. 2017;7:6013–7.

[29] Kang H, Hong SJ, Park M, Jang H-S, Nam K, Choi S, et al. Tuning the electronic structure of single-walled carbon nanotube by high-pressure H2 exposure. Nanotechnology. 2018;30:065201.

[30] Muster J, Kim CT, Krstev V, Park JG, Park YW, Roth S, et al. Electrical transport through individual vanadium pentoxide nanowires. Adv. Mater. 2000;12:420–4.

[31] Chen Z, Qin Y, Wang D, Xiao Q, Peng Y, Wang X, et al. Design and synthesis of hierarchical nanowire composites for electrolyrochemical energy storage. Adv. Funct. Mater. 2009;19:3420–6.

[32] Xiong C, Aliev AE, Gnad B, Balkus Jr KJ. Fabrication of silver vanadium oxide and V2O5 nanowires for electrochromics. ACS Nano 2008;2:293–301.

[33] Raddour-Hadjian R, Raebelboom E, Pereira-Ramos JP. New structural characterization of the Li1–xV2O5 system provided by Raman spectroscopy. Chem. Mater. 2006;18:3548–56.

[34] Lee S-H, Cheong HM, Seong MJ, Liu P, Tracy CE, Mascarenhas A, et al. Microstructure study of amorphous vanadium oxide thin films using Raman spectroscopy. J. Appl. Phys. 2002;92:1893–7.

[35] Kim BH, Yu HY, Hong WG, Park J, Jung SC, Nam Y, et al. Hydrogen spillover in Pd-doped V2O5 nanowires at room temperature. Chem. Asian J. 2012;7:684–7.

[36] Kim BH, Kim A, Oh S-Y, Bae S-S, Yun YJ, Yu HY. Energy gap modulation in V2O5 nanowires by gas adsorption. Appl. Phys. Lett. 2008;93:233101.

[37] Schilling O, Colbow K. A mechanism for sensing reducing gases with vanadium pentoxide films. Sens. Actuators B 1994;21:151–7.