Journal of Advanced Research 24 (2020) 205–209

Contents lists available at ScienceDirect

Journal of Advanced Research

journal homepage: www.elsevier.com/locate/jare

Interaction between V_2O_5 nanowires and high pressure CO_2 gas up to 45 bar: Electrical and structural study

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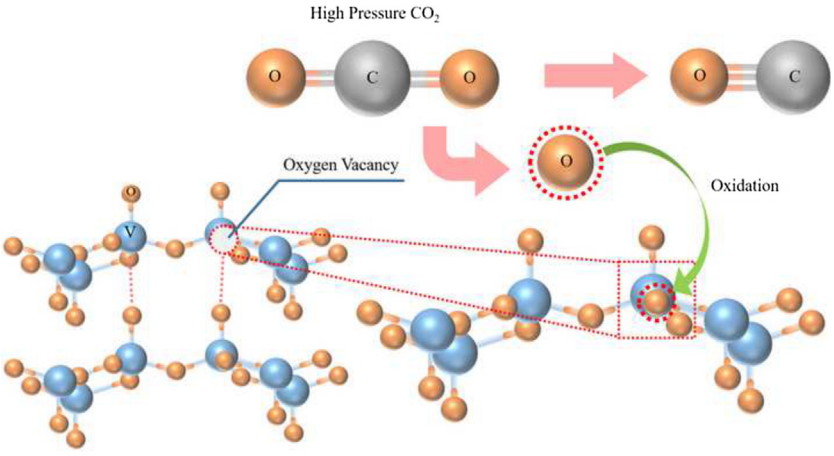
HIGHLIGHTS

- 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_3—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.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 October 2019
Revised 23 January 2020
Accepted 27 January 2020
Available online 30 January 2020

Keywords:
Carbon dioxide
High CO_2 pressure
Oxidative dehydrogenation
V_2O_5 Nanowire

ABSTRACT

In the oxidative dehydrogenation (ODH) process that converts ethylbenzene to styrene, vanadium-based catalysts, especially V_2O_5, are used in a CO_2 atmosphere to enhance process efficiency. Here we demonstrate that the activation energy of V_2O_5 can be manipulated by exposure to high pressure CO_2, using V_2O_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_3—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.

Peer review under responsibility of Cairo University.
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https://doi.org/10.1016/j.jare.2020.01.014
2090-1232/

Introduction

Carbon is the most fundamental element in ecological systems and biological organisms. The atmospheric concentration of carbon gas, particularly carbon dioxide (CO_2), is also known to be the one of the main factors driving climate change, global warming and ocean acidification. Nevertheless, 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 V_2O_5, the valence state of the vanadium switches back and forth between V^{4+} and V^{5+} as shown in Fig. 1 [21,22]. However, the persistent reduction of V^{5+} to V^{4+} results in catalyst deactivation. In other words, a large amount of V^{5+} compared with that of 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, CO_2 gas has become the preferred alternative oxidant, due to its advantages [1–7,12–20]. For example, in a 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 CO_2 than with superheated steam [24]. This is the reason for the growing industrial interest in 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 V_2O_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 V_2O_5 nanowires (VON) and investigated their structural modulation and electrical transport property as a function of 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 CO_2. We found an increase in the interlayer distance in the VON, and an increase in the V^{5+} state, after the VON were exposed to high 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 CO_2 atmosphere.

Experimental

Synthesis of the V_2O_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 50WX8-100, 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 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 CO_2 gas pressure using a home-made pressure chamber.

The VON film in the pressure chamber was heated at 80 ℃ and high vacuum condition (1.0×10^{-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% CO_2 gas was used. 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 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 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).

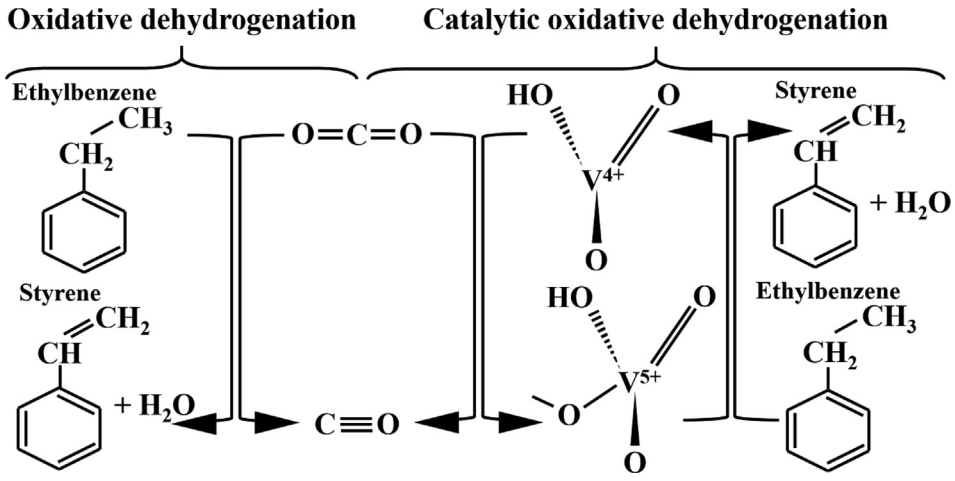

Fig. 1. Schematic for the mechanism of the ODH process of ethylbenzene with and without the presence of V_2O_5 as a catalyst.

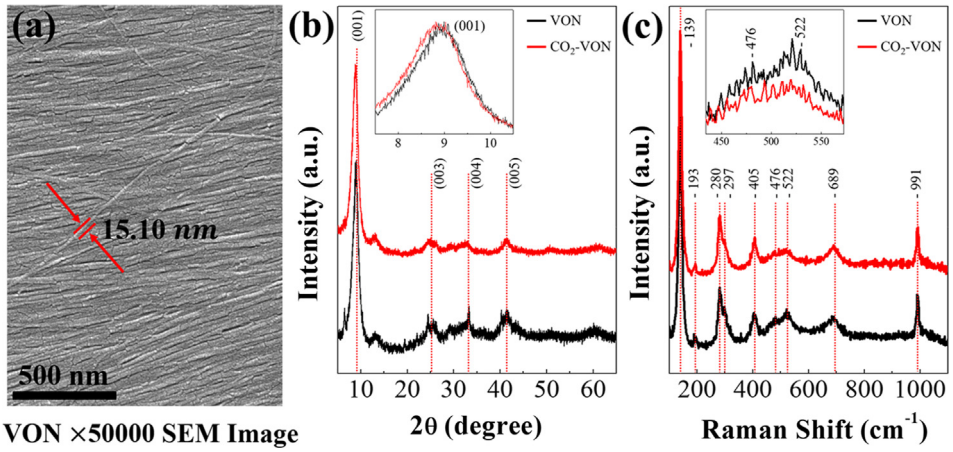

Fig. 2. (a) SEM Image of VON and (b) X-ray diffraction patterns and (c) Raman spectroscopy of VON and CO_2-VON.

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 CO_2 gas exposure (CO_2-VON) are shown in Fig. 2(b). The (0 0 1) peak of the CO_2-VON has shifted to a smaller angle (2θ = 8.88 for VON and to 8.75° for CO_2-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 CO_2 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 V_2O_5 units belonging to the unit cell. The peaks at 280 and 405 cm^{-1} are associated with the bending vibration of the V=O bonds. The peaks at 689 and 991 cm^{-1}, respectively, correspond to the bending vibration of doubly coordinated oxygen (V_2—O) and the stretching vibration mode of the shortest V—O_1. These six peaks did not change even after high CO_2 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 (V_3—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 CO_2 gas pressure (see Fig. S1 in Supplementary Information and the inset in Fig. 2(c)). This can be interpreted as follows. The amount of V—O—V and V_3—O bonds is relatively small due to oxygen vacancies in the pristine VON. After CO_2 exposure, the VON is oxidized. As a result, the amplitude of vibration in both bonds (phonon) is weakened. This effect can be seen in $G(P)$.

Electrical transport property of VON with respect to CO_2 gas pressure

Fig. 3 shows the electrical transport property of VON as a function of CO_2 gas pressure from vacuum (~10^{-6} Torr) to 45 bar. As soon as the VON was exposed to 5 bar of CO_2 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 CO_2 pressure. This behavior is similar to the oxygen pressure-dependent conductance of VON [37].

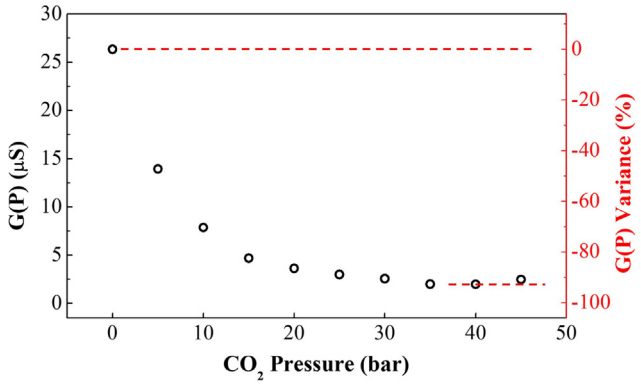

Fig. 3. CO_2-Pressure dependent $G(P)$ of VON from vacuum to 45 bar.

In general, charge transport in VON has been interpreted to be by small polaron hopping. The concentration ratio of $V^{4+}/(V^{4+} + V^{5+})$ plays an important role in this transport behavior [25]. Specifically, the amount of V^{4+} and V^{5+} 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 V^{5+}, producing V^{4+}, which can be understood as V^{5+} 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 CO_2 exposure

For this reason, the valence state of the vanadium in VON before and after exposure to CO_2 was studied using XPS (Fig. 4). The surveys of pristine VON and CO_2-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 $2p_{1/2}$, and V $2p_{3/2}$ (Fig. 4). The O1s peak consisted of three sub-peaks: V—OH at 533.29 eV, V—O—V at 531.65 eV, and O^{2+} at 530.29 eV. The amount of V—OH slightly increased after CO_2 exposure (Table 1). This shows that the surface OH rarely changes after annealing and CO_2 exposure.

On the other hand, the amount of V—O—V bonds in the VON after CO_2 exposure increased from 37.07 to 54.61%. V_2O_3, V_2O_5 (V^{5+}), and VO_2 (V^{4+}) species were observed in V $2p_{3/2}$. Note that the amount of V_2O_5 species significantly increased from 48.05%

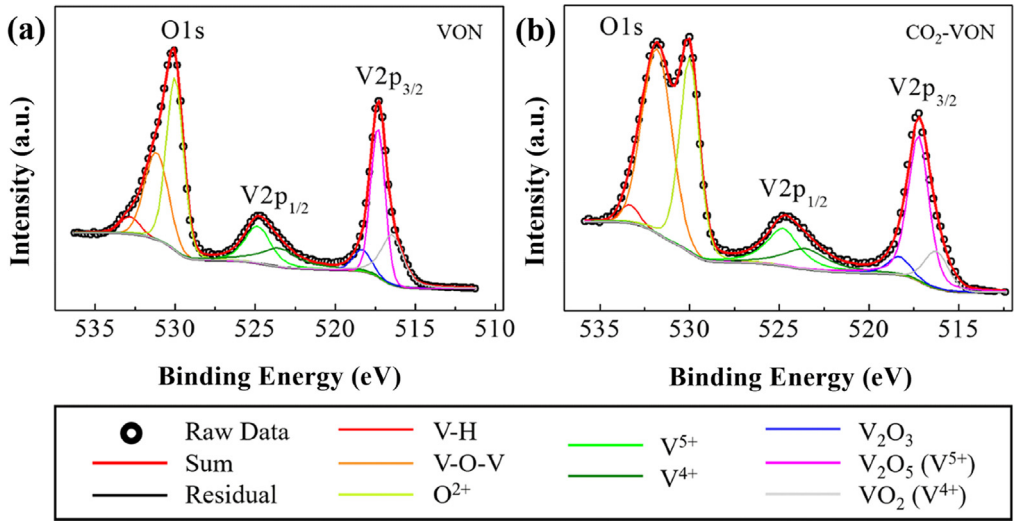

Fig. 4. X-ray photoelectron spectroscopy showing the O1s peak, V $2p_{1/2}$ peak, and V $2p_{3/2}$ peak in (a) VON and (b) CO_2-VON.

Table 1
Atomic concentration in VON and CO_2-VON obtained from the XPS results.

Peak List and chemical species (Position/In-region ratio)		VON		CO_2-VON	
O1s	**V-OH**	533.29 / 1.69%	42.29%	533.33/3.34%	56.05%
	V-O-V	531.62/11.76%		531.82/54.61%	
	O^{2+}	530.29/86.54%		530.00/42.05%	
$V2p_{1/2}$	**V^{5+}**	524.80/26.99%	19.71%	524.82/57.26%	16.27%
	V^{4+}	523.70/73.01%		523.65/42.72%	
$V2p_{3/2}$	**V_2O_3**	518.03/6.23%	38.00%	518.31/9.94%	27.64%
	$V_2O_5(V^{5+})$	517.16/48.05%		517.24/71.89%	
	$VO_2(V^{4+})$	516.27/45.72%		516.25/18.18%	

for VON, to 71.89% for CO_2-VON, but the VO_2 species decreased from 45.72% to 18.18%.

Since the charge transport in VON is mainly governed by the amount of V^{4+} and V^{5+} as mentioned above, we focused on the vanadium species. The ratio of V^{4+}/V^{5+} changed from 0.952 for the pristine VON to 0.253 for CO_2-VON. The decrease in V^{4+}/V^{5+} in the VON after CO_2 exposure indicates that the VON was oxidized due to CO_2. A notable point is that $G(P)$ continuously decreased and saturated with the increase in CO_2 pressure. This means that the high CO_2 pressure enhanced the oxidation of the reduced VON.

Conclusions

This study investigated the effect of high CO_2 gas pressure on VON conductivity, and revealed that pressure-dependent oxidation intrinsically reduced the VON. $G(P)$ continuously decreased as CO_2 pressure increased, which resulted in an increase in V^{5+}. This behavior was confirmed by XPS taken before and after exposure to high CO_2 pressure. Upon CO_2 gas exposure, the ratio of V^{4+}/V^{5+} was reduced by four times. Structural modulation resulting from CO_2 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_3—O bonds. This study provides a potential method for improving the ODH process using a VON catalyst in a high-pressure CO_2 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-2017R1A1A1A05000789).

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.

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