

pubs.acs.org/JPCC

Adsorbed CO₂-Mediated CO₂ Photoconversion Cycle into Solar Fuel at the O Vacancy Site of Zirconium Oxide

Keisuke Hara, Misa Nozaki, Rumiko Hirayama, Rento Ishii, Kaori Niki,* and Yasuo Izumi*



contrast to the first-row transition-metal oxides. The COH and/or CO species transfer from ZrO_2 to Ni in a concerted mechanism was energetically favorable, and the apparent E_{act} value from hydroxycarbonyl species to methane was reduced to 0.67 eV.

1. INTRODUCTION

CO2 conversion into fuels utilizing natural light completes a new C neutral cycle.^{1,2} To achieve such solar fuels as a potential renewable energy source in a sustainable society, the understanding of reaction routes using good photocatalysts for solar fuel production is essential to improve the efficiency to be economically viable. Recently, selective methane photogeneration using a Ni-zirconium oxide photocatalyst was reported at a rate of 0.98 mmol $h^{-1} g_{catalyst}^{-1.3}$ The rate was one of the highest solar fuel production rates confirmed by the online isotopic monitoring of ¹³CO₂ and ¹³C-products.⁴

 $(E_{\rm act})$ of 2.6 eV, but the water desorption energy was greatly

compensated by the CO_2 adsorption energy at the $V_0^{\bullet\bullet}$ site, in

A pioneering study was reported for the photocatalytic CO₂ reduction pathway with an anatase-phase TiO₂(101) surface based on density functional theory (DFT) calculations using the climbing image-nudged elastic band (CI-NEB) method to propose a hydrogenation route maintaining the C-O unit (formaldehyde pathway) over the oxygen vacancy $(V_{\Omega}^{\bullet\bullet})$ site of TiO₂.⁵ The other possibility is the carbene pathway that is via dissociated C and carbene (CH₂).⁵ However, an essential question remains as to why ZrO₂ can photoconvert ¹³CO₂ into ¹³CO, while the other semiconductors, e.g., TiO₂, ZnO, and Cu_xO (x = 1, 2), often significantly form ¹²CO derived from adventitious C.6 To achieve sustainable energy and create a new carbon neutral cycle, the reason why ZrO2 exclusively forms ¹³C-labeled products using ¹³CO₂, not affected by adventitious $C_{1,2,7-14}$ except for CO₂ strongly adsorbed from the air was investigated.^{3,4} This paper reports the unexpected catalytic role of $V_0^{\bullet\bullet}$ sites on ZrO_2 and the detailed

photocatalytic reaction routes to CO and/or COH and further to CH₄ with the aid of Ni nanoparticles.

Energy compensated

2. METHODS

2.1. Experiments. Twenty milligrams of ZrO₂ [JRC-ZRO-3, Catalysis Society of Japan; major monoclinic and minor tetragonal phase; specific surface area (SA), 94.4 m² g⁻¹] powder was placed in a quartz U-tube connected to a Pyrex glass circulation system (206.1 mL) and treated in a vacuum for 1 h (10^{-6} Pa). H₂ gas (20 kPa; purity > 99.99%) was introduced, and the temperature was increased to 723 K, maintained for 10 min, and treated in a vacuum. Thereafter, ¹³CO₂ (2.3 kPa; ¹³C 99.0%, purity > 99.9%, Cambridge Isotope Laboratories, Inc., Tewksbury, MA) and H₂ (21.7 kPa) were introduced into the system and irradiated by UV-visible light using a 500 W Xe arc lamp (SX-UID502XAM, Ushio, Japan) through a quartz fiber light guide (Optel, Tokyo, Japan; Model 1.2S15-1000F-1Q7-SP-RX) for 48 h. The reaction gas was monitored by online gas chromatography-mass spectrometry (GC-MS; JMS-Q1050GC, JEOL, Tokyo, Japan).

Received: August 24, 2022 **Revised:** December 7, 2022 Published: January 19, 2023



Article



https://doi.org/10.1021/acs.jpcc.2c06048 J. Phys. Chem. C 2023, 127, 1776–1788

Subsequently, the reaction gas was evacuated for 1 min; natural CO₂ (0.67 kPa; ¹²CO₂ 98.9%) was introduced into the system, and the pressure changes of ¹²CO₂ and ¹³CO₂ gases were monitored by online GC-MS. In comparison, a photocatalytic test was performed under ¹³CO₂ and UV– visible light irradiation in the absence of a reductant.

2.2. Theoretical Calculations. Spin-polarized periodic DFT calculations were conducted using the Vienna Ab initio Simulation Package (VASP) code version 6.2.1^{15–18} computed on a VT64 Server XS2-2TI comprising four units of Intel Xeon Platinum 9242 Processors (2.3 GHz, 48 cores; Visual Technology, Tokyo, Japan). The projector-augmented wave method was employed at the DFT-D3 level¹⁹ to incorporate the van der Waals interaction. The generalized gradient approximation (GGA)-revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional²⁰ was employed by setting a plane-wave energy cutoff at 500 eV. Separately, each optimized structure at the D3 level employing the GGA-RPBE functional was further optimized by adding U(U = 4.0)eV) to the original functional. The geometry of each species starting from CO₂ to CO evolution and hydroxy on Zr and to CO evolution and hydroxy to occupy the $V_{\Omega}^{\bullet\bullet}$ site negligibly changed. The activation energy (E_{act}) values were essentially preserved independent of the functional difference. The detailed discussion on the charge distribution of transition state (TS) and the localized density of states is reported elsewhere (unpublished results).

The criterion convergence was set at 10^{-6} eV for the selfconsistent field cycle, and optimizations were regarded as converged when the forces on all atoms were smaller than 1.0 eV nm⁻¹. All of the atoms were fully relaxed at the structural optimization. The Brillouin zone was sampled with a 3 × 3 × 1 wave number vector *k*-point grid. The transition states were pursued using the CI-NEB method.²¹ Based on the wave functions obtained from the DFT calculations, the molecular orbital-projected density of states (MOPDOS) was simulated using the MOPDOS@VASP code²² compatible with the VASP package.

The monoclinic-phase $\text{ZrO}_2(111)$, (001), and ($\overline{111}$) surfaces comprising (2 × 2 × 2) element unit cells were chosen as a slab model with a vacuum spacing of 1.0 nm between the slabs (Chart 1a, c, and e). The surface oxygen vacancy site on $\text{ZrO}_2(\text{V}_0^{\text{o}})$ was modeled by removing an O atom at the top layer of the $\text{ZrO}_2(111)$, (001), and ($\overline{111}$) surfaces (Chart 1b, d, and f).

The crystal phase and exposed faces of these slab models were chosen based on the results of high-resolution transmission electron microscopy and X-ray diffraction measurements of the ZrO_2 photocatalyst combined with Ni (10 wt %) via the liquid-phase reduction method.³ Hemispherical Ni₁₉ clusters exposing the (111) face based on the face-centered cubic (fcc) structure of the Ni metal were used. The (111) surface of fcc Ni with (2 × 2 × 2) element unit cells was chosen as the slab model allowing a vacuum spacing of 1.0 nm between the slabs (Chart 2).

The formation energy $(E_{\text{formation}})$ of oxygen vacancy sites and the adsorption energy (E_{ads}) were calculated based on eqs 1 and 2, respectively

$$E_{\text{formation}} = E_{\text{V}_{\text{O}}} - E_{\text{slab}} + \mu_{\text{O}} \tag{1}$$

$$E_{\rm ads} = E_{\rm mol/slab} - E_{\rm mol} - E_{\rm slab}$$
(2)

pubs.acs.org/JPCC

Article





^{*a*}(a) Monoclinic $ZrO_2(111)$ faces with parameters of a = 1.35 nm, b =1.464 nm, c = 1.488 nm, $\alpha = 114.68^{\circ}$, $\beta = 61.79^{\circ}$, $\gamma = 116.44^{\circ}$, and 192 atoms comprising 64 ZrO₂ units with a 1.0 nm vacuum layer introduced in the direction of the x-axis. Green, Zr atom; red, O atom. (b) $V_0^{\bullet\bullet}$ sites on the $ZrO_2(111)$ face. Silver, O atom to be removed bound to two Zr atoms, thereby forming $(\mu$ -Zr)₂ and $(\eta$ -O)₂ adsorption orientations of CO2. Yellow, O atom to be removed bound to three Zr atoms, thereby forming $(\mu$ -Zr)₃ and $(\eta$ -O)₂ adsorption orientations of CO2. (c) ZrO2(001) faces with parameters of a = 1.03 nm, b = 1.05 nm, c = 1.07 nm, $\alpha = 90^{\circ}$, $\beta = 99.25^{\circ}$, $\gamma =$ 90°, and 96 atoms comprising 32 ZrO2 units with a 1.0 nm vacuum layer introduced in the direction of the z-Axis. (d) $V_0^{\bullet\bullet}$ sites on the ZrO₂(001) face. silver, O atom to be removed bound to two Zr atoms, thereby forming $(\mu$ -Zr)₂ and $(\eta$ -O)₂ adsorption orientations of CO₂. (e) ZrO₂(111) facets with parameters of a = 1.639 nm, b =1.489 nm, c = 1.469 nm, $\alpha = 53.82^{\circ}$, $\beta = 57.95^{\circ}$, $\gamma = 56.94^{\circ}$, and 192 atoms comprising 64 ZrO₂ units with a 1.0 nm vacuum layer introduced into the x-axis. (f) $V_0^{\bullet\bullet}$ sites on the $ZrO_2(\overline{111})$ face. Silver, O atom to be removed bound to two Zr atoms, thereby forming (μ - $Zr)_2$ and $(\eta$ -O)₂ adsorption orientations of CO₂. Yellow, O atom to be removed bound to three Zr atoms, thereby forming $(\mu$ -Zr)₃ and $(\eta$ -O)₂ adsorption orientations of CO₂ depicted using the VESTA Version 3.5.7.

Chart 2. Ni(111) Face with Parameters of a = 0.859 nm, b = 0.496 nm, and c = 0.607 nm and 32 Atoms and a 1.5 nm Vacuum Layer Introduced into the *z*-Axis Depicted Using the VESTA Version $3.5.7^{23}$



where $E_{\text{mol/slab}}$, $E_{\text{Vo'}}$, E_{mol} , E_{slab} , and μ_{O} are the total energy of the adsorbate on the slab model, the energies of the surface

comprising the O vacancy site, the isolated molecule in the gas phase and surface, and the chemical potential of O, respectively.

3. RESULTS AND DISCUSSION

3.1. ¹³CO₂ **Photoreduction.** The photoreduction of ¹³CO₂ into ¹³CO has been reported using ¹³CO₂, H₂, ZrO₂, and UV-visible light irradiation.^{3,4} Here, the formation rate was compared with that using ¹³CO₂, ZrO₂, and UV-visible light irradiation.

The ¹³CO formation rate was 0.80 μ mol h⁻¹ g_{cat}⁻¹ using ¹³CO₂ and H₂ and 0.28 μ mol h⁻¹ g_{cat}⁻¹ using ¹³CO₂ within 5 h of the reaction (Figure 1). Although the formation continued



Figure 1. Time-course reaction of ${}^{13}\text{CO}_2$ photoreduction irradiated with UV–visible light using ZrO₂ reduced at 723 K under ${}^{13}\text{CO}_2$ (2.3 kPa) and H₂ (21.7 kPa) (circles) and ${}^{13}\text{CO}_2$ (2.3 kPa) (squares). The amount of ZrO₂ was 0.020 g.

for 48 h using $^{13}\rm{CO}_2$ and H₂, the $^{13}\rm{CO}$ formation ceased at ~15 h of the reaction using $^{13}\rm{CO}_2$, suggesting that the reaction was not truly catalytic but just stoichiometric, e.g., the irreversible reaction with the V_0^{\circ\circ} site.

3.2. Isotope-Labeled CO₂ Uptake and Exchange. The time course of the ¹²CO₂ uptake and exchange that was monitored after the photocatalytic test using ¹³CO₂ and H₂ (Figure 1) is illustrated in Figure 2. The experimental reaction steps are illustrated in Scheme 1. Within 1 h of the reaction, ¹²CO₂ was rapidly adsorbed on the ZrO₂ surface at a rate constant of 8.0 h⁻¹. The amount was 8.2 μ mol per 20 mg of ZrO₂. Corresponding to the physisorption of ¹²CO₂, the physisorbed ¹³CO₂ during the photocatalytic test under ¹³CO₂,



Figure 2. Time-course uptake and exchange reaction of natural CO_2 ($^{12}CO_2$ 98.9%, 0.67 kPa) irradiated with UV–visible light using ZrO_2 reduced at 723 K under $^{13}CO_2$ (2.3 kPa) and H₂ (21.7 kPa) under UV–visible light for 48 h (Figure 1, circles). The amount of catalyst was 0.020 g.

Article

Scheme 1. (A) ¹³CO₂ and (B) ¹²CO₂ Exchange Reaction Mechanisms over the Oxygen Vacancy at the ZrO₂ Surface



H₂, and UV–visible light irradiation was desorbed at a rate constant of 3.0 h⁻¹, and the amount was 2.8 μ mol (Figure 2). Further, ¹³CO₂ desorption was significantly slower at a rate constant of 0.02 h⁻¹, and the amount was 3.0 μ mol. This should be the exchange of chemisorbed ¹³CO₂ on the V₀^{••} sites during the photocatalytic test with gas-phase ¹²CO₂ (Scheme 1B) comparable to a rate constant of 0.07 h⁻¹ for ¹²CO₂ desorption from the V₀^{••} sites for the fresh catalyst with gas-phase ¹³CO₂ (Scheme 1A).³

Based on the specific SA of ZrO_2 (94.4 m² g⁻¹), the density of such a chemisorption site of CO_2 on the $V_0^{\bullet\bullet}$ sites was calculated to be 0.96 in an area of 1 nm² at the ZrO_2 surface. Zhang et al. previously assigned 0.655 μ mol of ${}^{12}CO_2$ exchanged during the ${}^{13}CO_2$ uptake and exchange test related to O vacancy sites (Scheme 1A),³ which was only 22% of 3.0 μ mol of the ${}^{13}CO_2$ exchanged (Figure 2). The exchanged ${}^{12}CO_2$ originated from the ${}^{12}CO_2$ adsorbed from air on the V_0^{\bullet\circ} site of ZrO_2 ,^{3,4} but it was not fully occupied (Scheme 1A, top). In contrast, the ZrO_2 photocatalyst was only evacuated for 1 min after the ${}^{13}CO_2$ was preserved for this uptake and exchange test (3.0 μ mol; Scheme 1B).

3.3. Formation Energy of V₀[•] **Sites.** First, V₀[•] sites were formed on monoclinic $ZrO_2(001)$, (111), and (111) faces (Chart 1, b, d, and f). Based on eq 1, the formation energy was calculated to be 5.9–6.4 eV (Table 1). The major part of V₀[•]

Table 1. Formation Energy of Oxygen Vacancy Sites at $(\mu$ -Zr)₂ and $(\mu$ -Zr)₃ Sites of the Monoclinic ZrO₂ Surface

entry	surface	$E_{\rm formation}~({\rm eV})$
a	$(\mu$ -Zr) ₂ site on ZrO ₂ (001)	6.2
b	$(\mu$ -Zr) ₂ site on ZrO ₂ (111)	6.4
с	$(\mu$ -Zr) ₃ site on ZrO ₂ (111)	6.0
d	$(\mu$ -Zr) ₂ site on ZrO ₂ ($\overline{11}1$)	5.9
e	$(\mu$ -Zr) ₃ site on ZrO ₂ ($\overline{111}$)	5.9

sites was formed during the production process of the $\rm ZrO_2$ sample at the supplier (Daiichi Kigenso Kagaku Kogyo Co., Osaka, Japan),⁴ and the population increased by 47% with the $\rm H_2$ treatment at 723 $\rm K.^3$

3.4. CO₂ **Adsorption Geometry.** First, $V_0^{\circ\circ}$ sites were formed on monoclinic $ZrO_2(001)$, (111), and (111) faces (Table 1). Fast methane photoformation was achieved using a major monoclinic-phase ZrO_2 combined with Ni⁰ nanoparticles.³ Typically, three types of initial geometries exist for the adsorption structure optimization using VASP:^{15–18} the (i) vertical orientation of the CO₂ molecule axis versus the ZrO_2 surface within the proximity of the $V_0^{\circ\circ}$ site, (ii) bonding from

pubs.acs.org/JPCC

Scheme 2. (A) Proposed Reaction Pathways and (B) Energetics of CO₂ Photoreduction Energetically Facilitated by the Oxygen Vacancy at the ZrO₂ Surface



two surface Zr atoms $(\mu$ -Zr)₂ and two O atoms of CO₂ $(\eta$ -O)₂ orientations maintaining the CO₂ molecular axis parallel to the ZrO₂ surface and the C atom was within the proximity of the V^o₀ site, and (iii) $(\mu$ -Zr)₃ and $(\eta$ -O)₂ orientations maintaining the CO₂ molecular axis parallel to the ZrO₂ surface and the C atom was within the proximity of the V^o₀ site. Geometries (ii) and (iii) were associated with the V^o₀ site created by removing an O atom of coordination numbers to Zr, 2 and 3 (Chart 1b, silver and yellow positions, respectively).

Among them, the $(\mu$ -Zr)₂ and $(\eta$ -O)₂ orientations of CO₂ starting from the initial geometry (ii) on the monoclinic ZrO₂(111) surface were significantly stable (Scheme 2A(b) and Chart 3b), originating from the V₀^{\circ} site coordinated to two Zr atoms (Chart 1b, silver, Scheme 2A(a), and Chart 3a). The energy change upon adsorption (E_{ads}) was -3.9 eV (Table 2b and Scheme 2B(a,b)). The value was compared with -3.2 eV for the (μ -Zr)₃ site on ZrO₂(111) (Table 2c), originating from the V₀^{\circ} site coordinated to three Zr (Chart 1b, yellow); -2.6 eV for the (μ -Zr)₂ site on ZrO₂(001) (Table 2a), originating from the V₀^{\circ} site coordinated to two Zr (Chart 1d, silver); -2.8 eV for the (μ -Zr)₂ site on ZrO₂(111) (Table 2d), originating from the V₀^{\circ} site coordinated to two Zr (Chart 1f, silver); and -2.5 eV for the (μ -Zr)₃ site on ZrO₂(111) (Table 2d), originating from the V₀^{\circ} site coordinated to two Zr (Chart 1f, silver); and -2.5 eV for the (μ -Zr)₃ site on ZrO₂(111) (Table 2d), originating from the V₀^{\circ} site coordinated to two Zr (Chart 1f, silver); and -2.5 eV for the (μ -Zr)₃ site on ZrO₂(111) (Table 2d), originating from the V₀^{\circ} site coordinated to two Zr (Chart 1f, silver); and -2.5 eV for the (μ -Zr)₃ site on ZrO₂(111) (Table 2e), originating from the V₀^{\circ} site coordinated to two Zr (Chart 1f, silver); and -2.5 eV for the (μ -Zr)₃ adsorption of CO₂ was geometrically inhibited at the ZrO₂(001) surface (Chart 1c,d).

On all of the assumed $V_0^{\bullet\bullet}$ sites, the E_{ads} values for CO_2 adsorption were between -2.5 and -3.9 eV. This is because the $V_0^{\bullet\bullet}$ sites exist in the fresh ZrO₂ sample supplied to our

laboratory, and a CO₂ adsorption step on the V₀^{••} site was enough exothermically (Table 2). If we consider the combination of the V₀^{••} site formation energy with the CO₂ adsorption energy (Tables 1 and 2), the total energy changes were 3.6, 2.5, 2.8, 3.1, and 3.4 eV for the $(\mu$ -Zr)₂ sites on ZrO₂ (001) and ZrO₂(111), the $(\mu$ -Zr)₃ site on ZrO₂(111), and $(\mu$ -Zr)₂ and $(\mu$ -Zr)₃ sites on ZrO₂(111), respectively, demonstrating that the combined steps were endothermic in accord with the thermodynamic stability of CO₂.

Similarly, the removal of two-, three-, and four-coordinated O sites is discussed to create $V_0^{\bullet\bullet}$ sites at the tetragonal $ZrO_2(101)$ surface.²⁵ Furthermore, similar M-shaped CO_2 adsorption was recently reported at various $V_0^{\bullet\bullet}$ sites at an anatase $TiO_2(101)$,^{5,26} Ca^{2+} -doped monoclinic $ZrO_2(\overline{111})$,²⁷ and $Bi_2WO_6(010)$ surfaces.²⁸

For the most stable $(\mu$ -Zr)₂ and $(\eta$ -O)₂ orientations on ZrO₂(111), the C atom was relatively reduced based on the Bader charge (1.05; Table 2b), while the C atom at the most unstable $(\mu$ -Zr)₃ and $(\eta$ -O)₂ orientations on ZrO₂(111) was even more reduced (Bader charge 1.02; Table 2e), compared with that of the other orientation and/or ZrO₂ crystal face (1.05–1.10; Table 2a–d). The O–C–O angle was 116.87–132.06° with an M-shaped drawing. Although it is believed that the O–C–O angle and/or Bader charge correlated well with the E_{ads} value,²⁹ based on Table 2, the number of supporting Zr sites more closely correlated with the E_{ads} value; the $(\mu$ -Zr)₂ site led to a greater E_{ads} value rather than that of the $(\mu$ -Zr)₃ site.

pubs.acs.org/JPCC

Chart 3. Three-Dimensional Illustration of Surface Species (Scheme 2A) during CO_2 Photoreduction to CO over the $ZrO_2(111)$ Surface Depicted Using the OVITO Version 3.7.8.²⁴ Panels (a)–(o) Correspond to Species a–o, Respectively, in Scheme 2A



Table 2. Adsorption Energy, the Bader Charge, and the O– C–O Angle of $(\mu$ -Zr)₂ and $(\mu$ -Zr)₃ M-Shaped CO₂ Adsorption on Oxygen Vacancy Sites at the Monoclinic ZrO₂ Surface

entry	surface	E _{ads} (eV)	Bader charge of C	O–C–O angle
a	$(\mu$ -Zr) ₂ site on ZrO ₂ (001)	-2.6	1.08	132.06°
b	$(\mu$ -Zr $)_2$ site on ZrO $_2(111)$	-3.9	1.05	129.72°
с	$(\mu$ -Zr) ₃ site on ZrO ₂ (111)	-3.2	1.10	116.87°
d	$(\mu$ -Zr) ₂ site on ZrO ₂ $(\overline{11}1)$	-2.8	1.10	128.70°
e	$(\mu$ -Zr) ₃ site on ZrO ₂ ($\overline{11}1$)	-2.5	1.02	123.34°

3.5. Associative Mechanism. Next, the proton addition step and the effect of light irradiation were evaluated during the CO₂ dissociation processes starting from the most stable M-shaped (μ -Zr)₂ and (η -O)₂ orientations of CO₂ on the ZrO₂(111) surface (Scheme 2A(b)). The adsorbed CO₂ transformed into a hydroxycarbonyl species, OCOH (Scheme 2A(d) and Chart 3d), through H addition via the reaction of a photogenerated hole with split H from H₂ on ZrO₂ and/or spillover from the Ni⁰ nanoparticle site (Scheme 2A(c) and Chart 2c). Similar H spillover from the Ag site toward the anatase-phase TiO₂(001) and (101) surfaces has been reported.^{4,30}

The charge transfer was suggested during the reaction steps from ${\rm CO}_2$ adsorption to hydroxycarbonyl species formation

Table 3. Change of the Summation of Bader Charges on Surface Species on $(\mu$ -Zr)₂ Oxygen Vacancy Sites and Two μ -Zr Atoms at the Monoclinic ZrO₂ (111) Surface in the Absence/Presence of Ni Nanoparticle

entry	surface	none adsorbed	two μ-Zr atoms	CO ₂ adsorbed	two <i>µ</i> -Zr atoms	OCOH adsorbed	two μ-Zr atoms
		Schemes 2	A(a) and 3A(a)	Schemes 2A	A(b) and $3A(b)$	Schemes 2A	(d) and 3 A(d)
a	$V_0^{\bullet \bullet}$ site on ZrO_2		4.22	-1.16	5.12	-1.02	4.90
		Schemes 4 B(a')	A(a') and $3B(-$	Schemes 4A	(b') and $3B(b')$	Schemes 4A	(d') and 3B(d')
b	$V_{O}^{\bullet \bullet}(\mu\text{-}Zr)_{2}$ site on ZrO_{2} with the Ni nanoparticle		5.26	-1.33	5.32	-0.72	5.14

https://doi.org/10.1021/acs.jpcc.2c06048 J. Phys. Chem. C 2023, 127, 1776–1788 Scheme 3. Extent of Charge Transfer during the Reaction Steps from CO_2 Adsorption to the Formation of O-C-O-H Species (Schemes 2A(d) and 4A(d')) Using (A) ZrO_2 and (B) Ni-ZrO₂, Respectively



(Scheme 2A(a–d),B(a–d)). Upon the CO₂ adsorption, a net 1.16 negative charge based on the Bader charge was transferred from the ZrO₂ (111) surface to one molecule of CO₂ (Table 3a and Scheme 3A(b)), followed by the hydrogen addition and electron transfer forming hydroxycarbonyl species. The species was still charged by -1.02 based on the Bader charge owing to the charge transfer from the supporting V₀[•] site (Table 3a and Scheme 3A(d)). The net one negative charge transfer strongly implies the direction of the separated electron injection from the accumulated V₀[•] site and/or the O 2p orbital of ZrO₂ by the UV light irradiation to CO₂-derived surface species. Such a photocatalytic scenario is further discussed below based on the MOPDOS of hydroxycarbonyl species rather than via heat reaction mechanism.

The direction of charge transfer from the $V_0^{\bullet\bullet}$ site to CO_2 based on Bader charges was also confirmed by the DOS distribution for $V_0^{\bullet\bullet}$ -ZrO₂ comprising the $V_0^{\bullet\bullet}$ site below the Fermi energy level (E_F ; Supporting Information, Chart S1a) and the appearance of CO_2 lowest-unoccupied molecular orbital (LUMO) just below the E_F level by the CO_2 adsorption (Chart S1b).

MOPDOS (Chart 4A) was obtained by projecting the wave function of OCOH-ZrO₂ onto the wave function of the

isolated OCOH (Scheme 2A(d)) to extract the frontier orbitals of OCOH species among the total DOS. The total DOS (Chart 4B) is the sum of the DOS of all atoms in the system and was used to narrow the range for extracting the band structure described below. The band structure (Chart 4C) was derived using the unfolding method³¹ to correctly extract the supercell band structure. Partial charge density (Chart 4D) was obtained based on the valence band (VB) maximum, conduction band (CB) minimum, and two intermediate levels determined from the total DOS and band structure. The molecular orbitals of OCOH species hybridized with those of ZrO₂ were determined from Gaussian-based molecular orbitals³² (Chart 4E).

The energy interval was approximately 1.4 eV between the highest occupied molecular orbital (HOMO) of the OCOH species (Chart 4A,B) and CB of ZrO_2 . The LUMO and HOMO were the transformation from antibonding (π^*) e_{1u} and nonbonding e_{1g} orbitals of the straight CO₂ molecule by the presence of the H atom and the surface (Chart 4E(i,ii), respectively). Regarding the electronic configuration, the LUMO and HOMO of the OCOH species effectively overlapped with the 4d orbital of the right-hand side Zr (Chart 4D(ii),E(i,ii)), which is also the major component of

pubs.acs.org/JPCC

Article



the CB of ZrO_2 (Chart 4D(i)), suggesting the electron transfer from the right-hand-side Zr atom to the C atom of the OCOH species as evident from the smaller Bader charge on the C (Table 2b and Scheme 3A(d)).

The key reaction steps of photocatalysis are redox reactions by the separated electrons and holes in the semiconductor under the irradiation of ultraviolet (UV) and/or visible light.^{1,2} The above-suggested charge transfer from the $V_0^{\bullet\bullet}$ site to the CO₂-derived surface species (Scheme 3A and Chart 4) predicts the direction of the separated electron injection in clear contrast to the basically directionless motion of thermal electrons.³³

The plausible electron injection routes to hydroxycarbonyl species (Schemes 2A(d) and 3A(d)) should be (i) from VB to CB (gap 4.2 eV; Chart 4B) and then to LUMO, (ii) from VB to LUMO (gap 4.8 eV; Chart 4A,B), (iii) from the $V_0^{\bullet\bullet}$ site to CB (gap 1.4 eV) and then to LUMO, (iv) from the $V_0^{\bullet\bullet}$ site to LUMO (gap 2.0 eV), and (v) from HOMO to CB (gap 1.4 eV) and then to LUMO (Chart 4A–C). The DOS of the $V_0^{\bullet\bullet}$ site effectively mixed with that of hydroxycarbonyl HOMO

(Chart 4A), and the plausible route v requires electron compensation from ZrO_2 to the HOMO of surface species.

The energy gaps were calculated to be 1.4-4.8 eV, effectively exceeding thermal activation barrier, whereas concentrated UV light photon energy (3.1-6.2 eV) from the Xe arc light source used in the photocatalytic tests for ZrO₂ and Ni–ZrO₂^{3,4} enabled to exceed the energy gaps of 1.4-4.8 eV in accord with the photocatalytic scenario in this study rather than thermal catalysis. Thus, the MOPDOS approach associated with DFT calculations in this study nicely extracts the geometry and electronic structure of surface intermediate species in the reaction coordinate of the CO₂ photoreduction, probably similar to that disclosed by the state-of-the-art spectroscopy combined with DFT calculations.³⁴

The O(HO)C...Zr-coordinated structure (Scheme 2A(d)) should further change to interact more when the excited electron from the VB to CB flows into the LUMO of the surface state under the irradiation of UV light. As a plausible route, the C–O bond of the O–COH species dissociates to hydroxy species and CO evolution (Scheme 2A(d–f)). The TS was the square O–C–O–H species (Scheme 2A(e) and Chart 3e) resulting in hydroxy species over the left-hand-side Zr atom (Scheme 2A(f) and Chart 3f). The $E_{\rm act}$ value of this reaction path was 1.37 eV (Scheme 2B(d,e)). This path was enabled by the photogenerated electron excitation to the VB and then the injection to the OCOH species.

The associative route was favorable starting from CO_2 on the $(\mu$ -Zr)₂ site using ZrO₂(111), owing to the greater E_{ads} value of -3.9 eV, compared with that of -2.5 to -3.2 eV starting from CO₂ on the other site and/or on the other ZrO₂ crystal face (Table 2a–e).

The final state in the associative route left the hydroxy species neighboring the $V_0^{\circ \circ}$ site (Scheme 2A(f),B(f) and Chart 3f) that differed from the original $V_0^{\circ \circ}$ site that lacked the hydroxy species at the beginning of the reaction (Scheme 2A(a)). If secondary CO₂ reacted, the insertion reaction of the secondary CO₂ into the O–H bond to form bicarbonate (Schemes 2A(g) and 2B(g) and Chart 3g), and the filling of the $V_0^{\circ \circ}$ site by the terminal O atom of bicarbonate (Schemes 2A(h) and 2B(h) and Chart 3h), proceeded nearly spontaneously, compared with the C–O dissociation steps in which the E_{act} value was significant, 1.37 eV (Scheme 2B(d,e)).

Thereafter, similar to the primary CO_2 dissociation (Scheme 2A,B(e-f)), a square geometry comprising O-C-O-H was formed with the E_{act} value of 1.44 eV, transforming into hydroxy and OCO species vertically filling the $V_0^{\bullet\bullet}$ site (Scheme 2A(i),B(i) and Chart 3i). However, the dissociation of the C-O bond of the OCO species to desorb CO (Scheme 2A(j),B(j) and Chart 3j) required as much as an E_{act} of 2.43 eV (Scheme 2B(j)). Thus, the secondary CO_2 dissociation route was implausible.

3.6. Hopping Route of CO₂ Dissociation. The possibility of the lateral dissociative reaction route was evaluated in comparison to the associative route in the previous section. The key was the interatomic distance between the Zr and O atoms: 2.015 nm on the $ZrO_2(111)$ surface shorter by 0.064 nm (Chart 1a,b), compared with 2.079 nm on the $ZrO_2(001)$ surface around the V₀^{••} site (Chart 1c,d). The two routes were distinguished whether the H atom combined with the O atom on the other side before the O-C dissociation (associative route; Scheme 2A(e)) or the O-C bond in the OCOH species directly dissociated (hopping route; Scheme 2A(k),B(k)) and the left-hand-side O atom filled the V₀^{••} site, leaving the COH species. The COH species was stabilized on the bridging site between the O and Zr atoms by hopping from the terminal site on the Zr atom. The E_{act} value of the first O-C dissociation step was 1.30 eV, which was smaller, compared with 1.37 eV for the associative route (Scheme 2B(d-f,k)). Following the COH species in the hopping route, the H atom approached the C atom, thereby forming a formyl group, then hydroxy, and CO (Scheme 2A(l,m),B(l,m) and Chart 3l,m).

3.7. Shortcut in the Associative Route. The hopping mechanism appeared to be more plausible, compared with the associative mechanism based on the energy comparison of the O–C dissociation step, 1.30 eV (Scheme 2B(d,k)) versus 1.37 eV (Scheme 2B(d-f)), respectively. However, a shortcut was observed in the associative route following species d, e, and m via the direct $V_0^{\bullet\bullet}$ site occupation by the hydroxy species (Scheme 2A(d,e,m) and Chart 3d, e, and m). The E_{act} value of the step was minimal, 1.18 eV (Scheme 2B(d,e,m)). Thus, this shortcut associative route was the most plausible for CO₂ photoreduction on the ZrO₂ photocatalyst to CO.³

The direct participation of the $V_0^{\bullet\bullet}$ site in the CO₂ reduction has rarely been reported to occupy the $V_0^{\bullet\bullet}$ site by the O derived from CO₂ (Scheme 2A(k,m)), followed by the regeneration of the $V_0^{\bullet\bullet}$ site (see the next section). Instead, the contribution of the interband state between the band gap to the CO₂ reduction step was discussed regarding the $V_0^{\bullet\bullet}$ site at the Bi₂WO₆ (010) surface.²⁸

The bicarbonate species (Scheme 2A(g)) was predominantly detected by Fourier transform infrared (FTIR) spectroscopy under CO_2 photoreduction conditions.³ Most of the bicarbonate species detected by FTIR should be separated from the $V_0^{\bullet\bullet}$ site and accumulated, rather than form species h because the concentration of the $V_0^{\bullet\bullet}$ site was 0.96 in an area of 1 nm² at the ZrO₂ surface (see the Isotope-Labeled CO_2 Uptake and Exchange section).

3.8. Regeneration of V_0^{\bullet} Sites. The V_0^{\bullet} regeneration route was evaluated starting from the common hydroxy species m occupying the V_0^{\bullet} site independent of the CO₂ reduction route, associative, hopping, and shortcut associative routes (Scheme 2A(m) and Chart 3m).

First, the H species was supplied neighboring the hydroxy species via the reaction of the photogenerated hole and dissociated/spillover H (Scheme 2A(n),B(n) and Chart 3n). Water formation reaction from the species required the E_{act} of 2.61 eV (Scheme 2A(n-o),B(n-o)). Thus, this step was ratelimiting among the overall catalytic steps of CO₂ photoreduction using monoclinic ZrO₂. Fortunately, in view of catalysis, this route did not require the water desorption energy of as much as 5.60 eV (Scheme 2A(o,a),B(o,a) and Chart 3o,a) to regenerate the original species a. Instead, the adsorption energy of CO₂ on the V₀^{oo} site (3.90 eV) effectively compensated for the water desorption energy (5.60 eV). Thus, the water desorption required just 1.70 eV to restart the catalytic cycle from species b but not species a (Scheme 2B(a,b,o) and Chart 3a-o).

3.9. Theoretical and Experimental Evaluation of V₀^{••} Sites. The concentration of the $V_{O}^{\bullet \bullet}$ sites at the ZrO_{2} surface heated at 723 K under H₂ and evacuated at 295 K for 1 h was 0.655 μ mol per 20 mg of ZrO₂ based on the ¹³CO₂ exchange reaction (Scheme 1A).³ In contrast, the concentration of $^{13}\text{CO}_2$ chemisorbed on the $V_O^{\bullet\bullet}$ sites was monitored at the ZrO_2 surface heated at 723 K under H₂, exposed to ¹³CO₂, H₂, and UV-visible light irradiation for 48 h, evacuated for 1 min, and exposed to ${}^{12}CO_2$. The ${}^{13}CO_2$ amount desorbed (3.0 μ mol) per 20 mg of ZrO₂, which was 4.6 times the simple ¹²CO₂ desorption under ¹³CO₂ gas,³ corresponded to the full concentration of the 0.96 $V_0^{\bullet \bullet}$ sites in 1 nm² at the ZrO₂ surface during the ¹³CO₂ photoreduction test (Figure 2 and Scheme 1B). This scenario correlated with the proposed reaction mechanism illustrated in Scheme 2A that skipped vacant species a, but the CO₂ adsorption energy always compensated for the $V_0^{\bullet \bullet}$ site regeneration to desorb water.

The ¹³CO₂ photoreduction test was performed using ZrO_2 and the irradiation of UV–visible light in the absence of the reductant (H₂ or H₂O). The ¹³CO formation ceased at ~15 h of reaction and 0.085 μ mol of the ¹³CO formation, whereas constant ¹³CO formation was observed at a rate of 0.80 μ mol h⁻¹ g_{cat}⁻¹ using ¹³CO₂, H₂, ZrO₂, and UV–visible light irradiation (Figure 1). Thus, the reaction path of the direct dissociation of CO₂ in the absence of hydrogen (Scheme 2A(b,p),B(b,p)) was negligible.

Alternatively, the E_{act} value for water formation from species n to o (Scheme 2A) drastically decreased to 1.6 eV if the

Scheme 4. (A) Proposed Reaction Pathways and (B) Energetics of CO_2 Photoreduction Energetically Facilitated by the Oxygen Vacancy at the $ZrO_2(111)$ Surface Neighboring to the Ni Nanoparticle^{*a*}



^aEnergy changes for the simple ZrO₂(111) surface free from the Ni nanoparticle (Scheme 2) are also drawn in panel B for comparison.

original $V_0^{\bullet\bullet}$ site was on the edge between the $\text{ZrO}_2(111)$ and (001) faces (figure not shown), suggesting the catalytic role of specific $V_0^{\bullet\bullet}$ sites (unpublished results).

3.10. Interface Effects between ZrO_2 Surface and Ni⁰ Nanoparticle. The CO₂ adsorption and activation were also evaluated at the interface between the $ZrO_2(111)$ surface and Ni(111) surface (Scheme 4). The orientation of the Ni cluster and V₀^o site on the $ZrO_2(111)$ surface is depicted in Chart S2A. Further details of the position of the (μ -Zr)₂-V₀^o site and the orientation of the Ni nanoparticle are also shown in Chart S2B. The E_{ads} value of CO₂ became smaller to -1.9 eV by the effect of the neighboring Ni nanoparticle compared to -3.9 eV for CO₂ on the ZrO₂ (111) surface free from Ni (Schemes 2B(a,b) and 4B(a',b') and Chart S3a',b').

The energy levels during the following reaction steps to hydroxycarbonyl and OCH species (Scheme 4A(a'-d') and Chart S3a'-d') were essentially in parallel separated by the difference of E_{ads} value (2.0 eV, Scheme 4B(a-d),(a'-d') and Chart S3(a'-d')); however, the E_{act} value from hydroxycarbonyl and OCH species (Scheme 4(d',s) and Chart S3(d',s)) was 0.32 eV at the interface between ZrO₂ and Ni nanoparticle (Scheme 4B(d',s)), significantly smaller compared to 1.37 eV in the associate route, 1.30 eV in the hopping route, and 1.18 eV in the associative, shortcut route (Scheme 2A), because COH species was significantly more stable on the Ni(111) surface [Scheme 4A(s) and Chart S3-TS from d'-s,s] compared to that on the $ZrO_2(111)$ surface (Scheme 2A(k)), and the intersection of potential curves for OCOH and COH species in the reaction coordinate was lowered more on the Ni (111) surface. The above discussion strongly suggested the critical photocatalytic role of the interface site between the ZrO₂ surface and Ni for the CO₂ photoreduction.

In contrast to the charge transfer from the $V_0^{\bullet\bullet}$ site at the ZrO_2 (111) surface to CO_2 (Scheme 3A), a net 1.04 negative charge transferred from the $V_0^{\bullet\bullet}$ site at the ZrO_2 surface to the Ni cluster (Table 3a,b and Scheme 3B(a')). Then, a net 1.33 negative charge based on the Bader charge was transferred from the Ni cluster to one molecule of CO_2 (Table 3b and Scheme 3B(b')), followed by the hydrogen addition and electron transfer forming hydroxycarbonyl species (Scheme 3B(c',d')). The species was still charged by -0.72 based on

the Bader charge owing to the charge transfer from the Ni cluster; however, the species almost combined with the Ni nanoparticle (Table 3b and Scheme 3B(d')).

As the OCOH species almost shared electrons with the Ni nanoparticle, the charge on Ni relatively increased compared to the state that CO_2 adsorbed on the ZrO_2 surface (Scheme 3B(b',d') and Table 3b). The DOS distribution between the E_F level and -2.5 eV for V_0° - ZrO_2 comprising V_0° (Chart S1c) increased by the CO_2 adsorption in the proximity of the Ni nanoparticle (Chart S1d), supporting the electron transfer from the V_0° site to the Ni nanoparticle and then to CO_2 -derived species. Thus, the photocatalytic reaction mechanism was partially tuned by the presence of Ni in the proximity of the V_0° site.

MOPDOS was also obtained by projecting the wave function of OCOH–Ni–ZrO₂ onto the wave function of isolated OCOH (Scheme 4A(d')) to extract the frontier orbitals of OCOH species among the total DOS. The total DOS (Chart 5B) is the sum of the DOS of all atoms in the system. Smaller DOS of isolated OCOH, especially in the similar energy range to the DOS of the Ni cluster, was successfully projected (Chart 5A). Because the hydroxycarbonyl species effectively shared electrons with the Ni cluster (Table 3b and Chart 5C), the OCOH LUMO was at 1.2 eV (Chart 5A) compared to the OCOH LUMO (Up spin) at 1.8 eV on the $ZrO_2(111)$ surface free from Ni (Chart 4A).

Partial charge density (Chart 5C) was obtained based on the VB maximum, CB minimum, and two intermediate levels determined from the total DOS and band structure. Similar to the results for the OCOH–ZrO₂ system (Chart 4D,E), the LUMO and HOMO were the transformation from antibonding (π^*) e_{1u} and nonbonding e_{1g} orbitals of the straight CO₂ molecule by the presence of the H atom and the surface (Chart 5C(i,ii), respectively). As was evident in the charge-transfer evaluation (Scheme 3B(d')), the LUMO and HOMO of the OCOH species effectively overlapped with the 3d orbital of the Ni cluster.

3.11. Hydrogenation of CO/Formate over Ni⁰ Nanoparticle. The ¹³CO formation rate using ¹³CO₂, H₂, ZrO₂ (20 mg), and UV–visible light irradiation (0.016 μ mol h⁻¹, Figure 1) and that using ¹³CO₂, ZrO₂ (20 mg), and UV–visible light

Chart 5. (A) MOPDOS, (B) Total DOS, and (C) Partial Charge Density of OCOH-Ni-ZrO₂(111) (Scheme 4A(d'))



irradiation (0.0057 μ mol h⁻¹ until 15 h of reaction; Figure 1) was quite low if 3.0 μ mol of V₀^{••} sites were utilized per 20 mg of ZrO₂ (Scheme 1). This fact does not contradict the efficient reaction path from CO₂ to CO, as revealed in Scheme 2A, e.g., via the M-shaped adsorption of CO₂ (label b), H-assisted O–C bond dissociation through the square intermediate of OCOH (labels c, d, and e), and occupation of the V₀^{••} site by hydroxy species (label m).

The H addition on the O atom neighboring the M-shaped adsorbed CO₂ (Scheme 2A(c) and Chart 3c) should have been accelerated by the H spilled over from the Ni nanoparticle that easily activated H₂.³ Thus, the ¹³CH₄ formation rate using ¹³CO₂, H₂, Ni⁰ (10 wt %)–ZrO₂ (20 mg), and UV–visible light irradiation (20 μ mol h⁻¹)³ accounted for one turnover per 9.2 min over the V₀^o site of the ZrO₂ surface to CO, formate, and/or COH that were rapidly converted into methane using the Ni⁰ nanoparticle surface.

In this context, the transfer of evolved CO (Scheme 2A(ef,i–j,l–m), and from e to m) from the ZrO_2 surface to the Ni⁰ nanoparticle was evaluated assuming the thermodynamically most stable and active Ni(111) surface.³⁵ Because the evaluation results (geometry, energy, and charge distribution of the surface intermediate species) negligibly changed whether on a simple Ni(111) surface (Scheme 5A(qz),B(q-z) and Chart S4q-z) or the Ni(111) neighboring to the ZrO₂(111) surface (Scheme 4A(s-x),B(s-x) and Chart S3s-x), the calculated results on the simple Ni(111) surface were basically enough. The formation rates of hydrocarbons, e.g., methane, from CO₂ using pristine transition-metal oxide semiconductors are insufficient for practical applications.^{1-3,} Thus, the understanding of the latter part of the reduction route, e.g., from CO/COH to hydrocarbons utilizing combined noble metals and/or first-row transition metal, is

Scheme 5. (A) Proposed Reaction Mechanism and (B) Energetics of CO_2 Photoreduction over the Ni(111) Surface Combined with ZrO_2



essential, rather than slower photocatalysis exclusively using transition-metal oxides, e.g., the formaldehyde pathway⁵ compared to their composites with noble metals and/or first-row transition metal (Figure 1). It should be noted that the formyl species was extremely unstable and easily transformed into carbonyl and H species over the Ni surface similar to the decomposition over the ZrO₂(111) surface (Scheme 2A(l,m)). Such a reactant transfer at the surface between a semiconductor metal oxide and supported metal nanoparticle was reported.³⁶

Using the Ni(111) surface (Chart 2 and Scheme 5A(q),B-(q),B(q)), H₂ activation to H atoms was essentially spontaneous;³⁵ however, the H addition to the O atom of the adsorbed CO to form COH species (Scheme 5A(r,s)) required a maximum $E_{\rm act}$ value of 1.72 eV (Scheme 5B(r,s)). As the reverse reaction discussed above for formyl species decomposition, the H addition to the C atom of adsorbed CO (Scheme 5A(r)) to form formyl species hardly occurred.

In contrast to the fact that the C-O bond dissociation of COH species to C and hydroxy species and then CH and hydroxy species (Scheme 5A(s,y,z)) were disadvantageous due to the E_{act} value of the step 2.06 eV (Scheme 5B(s,y,z)), the transformation from COH species into hydroxymethin (Scheme 5A(s,t)) easily proceeded with an E_{act} value of 0.72 eV (Scheme 5B(s,t)). The E_{act} value from hydroxymethin to methin (Scheme 5A(t,u)) was 1.45 eV (Scheme 5B(t,u)). The alternative route from hydroxymethin to hydroxycarbene (hydrogenation) and then to methin (dehydration; Scheme 5A(t,u',u)) was essentially energetically the same as the direct route from hydroxymethin to methin (Scheme 5B(t,u',u)). On the other hand, the route from hydroxymethin to hydroxycarbene and then to carbene (hydrogenative dehydration; Scheme 5A(t,u',v)) was implausible due to the greater E_{act} value for the latter step of 1.77 eV (Scheme 5B(t,u',v)). Experimentally, CO and methyl species (Scheme 5A(r,w)) were observed on the metallic Ni⁰ surface using FTIR. Therefore, it is reasonable to consider the following

apparent
$$E_{act}(1.09 \text{ eV})$$

= (*E* of the TS between species t and u and/or species u'

and u)
$$-$$
 (*E* of species q) (3)

Furthermore, the apparent E_{act} value needs to be considered at the interface site between ZrO_2 and Ni (Scheme 4B)

apparent
$$E_{\rm act}(0.67 \text{ eV})$$

The value over the Ni surface (1.09 eV) decreased to 0.67 eV at the interface between ZrO_2 and Ni, close to the apparent E_{act} value for methane formation from CO_2 and H_2 (0.58 eV) measured in the absence of light irradiation.³ In this sense, the evaluated reaction routes (Scheme 5) were not purely activated by Ni only but also affected by the ZrO_2 surface (Scheme 4).

In the whole reaction pathway from CO₂ to methane, the $V_0^{\bullet\bullet}$ site recovery step was rate-limiting (Scheme 2A(n,o),B-(n,o),B(n,o)); however, the E_{act} value of the first O–C bond dissociation step for hydroxycarbonyl species reduced from 1.18 eV via associate, shortcut route over the ZrO₂(111) surface (Scheme 2B(d,e,m)) to 0.32 eV via the interface

transfer of hydroxycarbonyl on ZrO_2 to COH species on Ni (Scheme 4B(d',s)). The apparent E_{act} value on Ni⁰ sites also decreased from 1.09 eV (eq 3) to 0.67 eV (eq 4) over the Ni(111) surface in the absence and presence of neighboring Ni sites (Scheme 5B(q,t,u,u') and 4B(d',t,u)), respectively, followed by the subsequent progressive hydrogenation from carbene to methane (Schemes 4A(v-x),B(v-x) and 5A(v-x)B(v-x)).

In other words, the transfer of hopped COH species (Scheme 2A(k) and Chart 3k) and/or the intermediate COH species that can be formed from the square HOCO intermediate to fill the O atom in the V_0° site via the shortcut associative route (Scheme 2A(e,m)) could explore a further shortcut to methane from Scheme 2A(k) and/or between species e and m to Scheme 5A(s), reducing the first hill of 1.72 eV over the Ni(111) surface (Scheme 5B(r,s)) to 0.32 eV at the interface between the $ZrO_2(111)$ surface and Ni(111) surface (Scheme 4B-d',s and TOC Graphic).

4. CONCLUSIONS

The presence of $V_0^{\bullet\bullet}$ sites over the ZrO_2 surface was verified by the isotopic exchange reaction of gaseous CO_2 under the irradiation of UV–visible light. Using ¹³CO₂ gas and ZrO_2 (20 mg), 0.655 μ mol of ¹²CO₂ was exchanged at a rate constant of 0.07 h⁻¹, suggesting that CO₂ adsorbed from air to the $V_0^{\bullet\bullet}$ sites. The population was 0.21 in the area of 1 nm² at the ZrO₂ surface. Conversely, isotopic exchange reaction of ¹²CO₂ was also performed under the irradiation of UV–visible light using ZrO₂ photocatalyst (20 mg) just after the photocatalytic test under ¹³CO₂, H₂, and UV–visible light. ¹³CO₂ (3.0 μ mol) was exchanged at a rate constant of 0.02 h⁻¹. Thus, the population of $V_0^{\bullet\bullet}$ sites was 0.96 in the area of 1 nm² at the ZrO₂ surface. The photocatalytic reduction of CO₂ did not proceed using CO₂ only as the reactant, but reducing agent, e.g., H₂, was indispensable.

The overall photocatalytic reaction pathway was evaluated from CO₂ to methane utilizing the Ni-ZrO₂ composite. The $V_0^{\bullet\bullet}$ sites as confirmed by experiments, particularly at the monoclinic $ZrO_2(111)$ surface, were effective for the stable adsorption of CO_2 as an M shape. The adsorption energy was between -2.5 and -3.9 eV depending on the site and ZrO_2 crystal face; however, the total steps of the formation of the $V_0^{\bullet\bullet}$ site as well as the CO₂ adsorption was in fact endothermic. The associate route via hydroxycarbonyl (OCOH) species forming a square intermediate to fill the $V_{\Omega}^{\bullet \bullet}$ site by hydroxy species was the most energetically favorable. The regeneration of the $V_0^{\bullet \bullet}$ site required the greatest E_{act} (2.61 eV); however, the greater adsorption energy of CO_2 on the site partially compensated for the water desorption energy, different from the photocatalytic energetics using first-row transition-metal oxides. The O-C bond dissociation of hydroxycarbonyl even decreased from 1.18 eV via associate, shortcut route over the $ZrO_2(111)$ surface to 0.32 eV via the interface transfer of hydroxycarbonyl on the $ZrO_2(111)$ surface to COH species stabilized more on the Ni(111) surface. The apparent E_{act} value on Ni⁰ sites also decreased from 1.09 to 0.67 eV over the Ni(111) surface in the absence and presence of the neighboring Ni nanoparticle, respectively. Thus, the interface transfer of CO/COH species was the key to the whole reaction pathway from CO₂ to methane over the Ni-ZrO₂ photocatalyst.

(4)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c06048.

Density of states for ZrO_2 comprising V_0^{o*} site and/or Ni nanoparticle in the absence/presence of CO_2 and threedimensional illustration of the Ni cluster and O vacancy site as well as the surface species over the Ni– $ZrO_2(111)$ surface or over the Ni(111) surface during CO_2 photoreduction, available free of charge (docx) (PDF)

AUTHOR INFORMATION

Corresponding Authors

Kaori Niki – Department of Chemistry, Graduate School of Science, Chiba University, Chiba 263-8522, Japan; Phone: +81-43-290-3699; Email: niki@chiba-u.jp

Yasuo Izumi – Department of Chemistry, Graduate School of Science, Chiba University, Chiba 263-8522, Japan;
orcid.org/0000-0001-8366-1864; Phone: +81-43-290-3696; Email: yizumi@faculty.chiba-u.jp; Fax: +81-43-290-2783

Authors

- Keisuke Hara Department of Chemistry, Graduate School of Science, Chiba University, Chiba 263-8522, Japan
- Misa Nozaki Department of Chemistry, Graduate School of Science, Chiba University, Chiba 263-8522, Japan

Rumiko Hirayama – Department of Chemistry, Graduate School of Science, Chiba University, Chiba 263-8522, Japan Rento Ishii – Department of Chemistry, Graduate School of

Science, Chiba University, Chiba 263-8522, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.2c06048

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Grant-in-Aid for Scientific Research B (20H02834, Y.I.) and C (17K05961, Y.I.; 20K05643, K.N.) from the Japan Society for the Promotion of Science and from the Establishment of University Fellowships toward the Creation of Science and Technology Innovation from Japan Science and Technology Agency (JPMJFS2107, K.H.&M.N.). Part of the calculations was executed at the Supercomputer Center, the Institute for Solid State Physics, the University of Tokyo, Japan.

REFERENCES

(1) Izumi, Y. Recent advances in photocatalytic conversion of carbon dioxide into fuels with water and/or hydrogen using solar energy and beyond. *Coord. Chem. Rev.* **2013**, *257*, 171–186.

(2) Izumi, Y.Recent Advances (2012–2015) in the Photocatalytic Conversion of Carbon Dioxide to Fuels Using Solar Energy: Feasibility for a New Energy, in ACS Books "Advances in CO_2 Capture, Sequestration, and Conversion". In Advances in CO_2 Capture, Sequestration, and Conversion; Jin, F.; He, L.-N.; Hu, Y. H., Eds.; ACS Symposium Series; ACS Publications, 2015; Vol. 1194, pp 1–46. DOI: 10.1021/bk-2015-1194.ch001.

(3) Zhang, H.; Itoi, T.; Konishi, T.; Izumi, Y. Efficient and Selective Interplay Revealed: CO_2 Reduction to CO over ZrO_2 by Light with

Further Reduction to Methane over Ni⁰ by Heat Converted from Light. Angew. Chem., Int. Ed. **2021**, 60, 9045–9054.

(4) Zhang, H.; Itoi, T.; Konishi, T.; Izumi, Y. Dual Photocatalytic Roles of Light: Charge Separation at the Band Gap and Heat via Localized Surface Plasmon Resonance To Convert CO_2 into CO over Silver–Zirconium Oxide. *J. Am. Chem. Soc.* **2019**, *141*, 6292–6301.

(5) Ji, Y.; Luo, Y. New Mechanism for Photocatalytic Reduction of CO_2 on the Anatase TiO_2 (1 0 1) Surface: The Essential Role of Oxygen Vacancy. J. Am. Chem. Soc. **2016**, 138, 15896–15902.

(6) Zhang, H.; Izumi, Y. Why Is Water More Reactive Than Hydrogen in Photocatalytic CO₂ Conversion at Higher Pressure? Elucidation by Means of X-Ray Absorption Fine Structure and Gas Chromatography-Mass Spectrometry. *Front. Chem.* **2018**, *6*, No. 408. (7) Li, K.; Peng, B.; Peng, T. Recent Advances in Heterogeneous Photocatalytic CO₂ Conversion to Solar Fuels. *ACS Catal.* **2016**, *6*, 7485–7527.

(8) Yang, C. C.; Yu, Y.-H.; van der Linden, B.; Wu, J. C. S.; Mul, G. Artificial Photosynthesis over Crystalline TiO_2 -Based Catalysts: Fact or Fiction? *J. Am. Chem. Soc.* **2010**, *132*, 8398–8406.

(9) Teramura, K.; Tanaka, T. Necessary and Sufficient Conditions for the Successful Three-Phase Photocatalytic Reduction of CO_2 by H₂O over Heterogeneous Photocatalysts. *Phys. Chem. Chem. Phys.* **2018**, 20, 8423–8431.

(10) Wang, S.; Hou, Y.; Wang, X. Development of a Stable $MnCo_2O_4$ Cocatalyst for Photocatalytic CO_2 Reduction with Visible Light. ACS Appl. Mater. Interfaces **2015**, 7, 4327–4335.

(11) Kar, P.; Zeng, S.; Zhang, Y.; Vahidzadeh, E.; Manuel, A.; Kisslinger, R.; Alam, K. M.; Thakur, U. K.; Mahdi, N.; Kumar, P.; Shankar, K. High Rate CO₂ Photoreduction Using Flame Annealed TiO₂ Nanotubes. *Appl. Catal.*, B **2019**, 243, 522–536.

(12) Ulagappan, \overline{N} .; Frei, H. Machanistic Study of CO₂ Photoreduction in Ti Silicalite Molecular Sieve by FT-IR Spectroscopy. J. Phys. Chem. A **2000**, 104, 7834–7839.

(13) Hameed, Y.; Gabidullin, B.; Richeson, D. Photocatalytic CO₂ Reduction with Manganese Complexes Bearing a κ^2 -PN Ligand: Breaking the α -Diimine Hold on Group 7 Catalysts and Switching Selectivity. *Inorg. Chem.* **2018**, *57*, 13092–13096.

(14) Boston, D. J.; Xu, C.; Armstrong, D. W.; MacDonnell, F. M. Photochemical Reduction of Carbon Dioxide to Methanol and Formate in a Homogeneous System with Pyridinium Catalysts. *J. Am. Chem. Soc.* **2013**, *135*, 16252–16255.

(15) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558–561.

(16) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid–Metal–Amorphous–Semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, *49*, 14251–14269.

(17) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energt Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.

(18) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(19) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. J. Comput. Chem. 2011, 32, 1456–1465.

(20) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved Adsorption Energies within Density-Functional Theory Using Revised Perdew–Burke–Ernzerhof Functionals. *Phys. Rev. B* **1999**, *59*, 7413–7421.

(21) Henkelman, G.; Jonsson, H. Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points. *J. Chem. Phys.* **2000**, *113*, 9978–9985.

(22) Lüftner, D.; Wei β , S.; Yang, X.; Hardax, P.; Feyer, V.; Gottwald, A.; Koller, G.; Soubatch, S.; Puschnig, P.; Ramsey, M. G.; Tautz, F. S. Understanding the Photoemission Distribution of Strongly Interacting Two-Dimensional Overlayers. *Phys. Rev. B.* **2017**, *96*, No. 125402.

(23) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology data. J. Appl. Cryst. 2011, 44, 1272–1276.

(24) Stukowski, A. Visualization and Analysis of Atomistic Ssimulation Data with OVITO-the Open Visualization Tool. *Modell. Simul. Mater. Sci. Eng.* **2010**, *18*, No. 015012.

(25) Puigdollers, A. R.; Illas, F.; Pacchioni, G. Structure and Properties of Zirconia Nanoparticles from Density Functional Theory Calculations. J. Phys. Chem. C 2016, 120, 4392–4402.

(26) Li, Z.; Zhang, L.; Huang, W.; Xu, C.; Zhang, Y. Photothermal Catalysis for Selective CO_2 Reduction on the Modified Anatase TiO_2 (1 0 1) Surface. ACS Appl. Energy Mater. **2021**, *4*, 7702–7709.

(27) Souza, E. F.; Appel, L. G. Oxygen Vacancy Formation and Their Role in the CO_2 Activation on Ca Doped ZrO_2 Surface: An Ab-Initio Study. *Appl. Surf. Sci.* **2021**, *553*, No. 149589.

(28) Liu, T.; Li, H.; Gao, J.; Ding, S.; Liu, X.; Jia, H.; Xue, J. Effect of Oxygen Vacancies on the Photocatalytic CO₂ Reduction Performance of Bi₂WO₆: DFT and Experimental Studies. *Appl. Surf. Sci.* **2022**, *579*, No. 152135.

(29) Nakamura, S.; Hatakeyama, M.; Wang, Y.; Ogata, K.; Fujii, K.A Basic Quantum Chemical Review on the Activation of CO₂. In *Advances in CO*₂ *Capture, Sequestration, and Conversion*; Jin, F.; He, L.-N.; Hu, Y. H., Eds.; ACS Books: Washington, D. C.1194; Chapter 5, pp 123–134.

(30) Hu, J.; Kim, E. M.; Janik, M. J.; Alexopoulos, K. Hydrogen Activation and Spillover on Anatase TiO₂-Supported Ag Single-Atom Catalysts. *J. Phys. Chem. C* **2022**, *126*, 7482–7491.

(31) Medeiros, P. V. C.; Tsirkin, S. S.; Stafström, S.; Björk, J. Unfolding Spinor Wave Functions and Expectation Values of General Operators: Introducing the Unfolding-Density Operator. *Phys. Rev. B* **2015**, *91*, No. 041116.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.et al.*Gaussian 09*, revision A. 2; Gaussian, Inc.: Wallingford CT, USA, 2016.

(33) Clavero, C. Plasmon-Induced Hot-Electron Generation at Nanoparticle/Metal-Oxide Interfaces for Photovoltaic and Photo-catalytic Devices. *Nat. Photonics* **2014**, *8*, 95–103.

(34) Li, X.; Wang, S.; Li, L.; Sun, Y.; Xie, Y. Progress and Perspective for In Situ Studies of CO₂ Reduction. J. Am. Chem. Soc. **2020**, 142, 9567–9581.

(35) Kresse, G. Dissociation and Sticking of H_2 on the Ni (1 1 1), (1 0 0), and (1 1 0) Substrate. *Phys. Rev. B* **2000**, *62*, 8295–8305.

(36) Yang, J.-J.; Zhang, Y.; Xie, X.-Y.; Fang, W.-H.; Cui, G. Photocatalytic Reduction of Carbon Dioxide to Methane at the Pd-Supported TiO_2 Interface: Mechanistic Insights from Theoretical Studies. ACS Catal. **2022**, 12, 8558–8571.

Article

Recommended by ACS

Electron Paramagnetic Resonance Quantifies Hot-Electron Transfer from Plasmonic Ag@SiO₂ to Cr⁶⁺/Cr⁵⁺/Cr³⁺

Constantinos Moularas, Yiannis Deligiannakis, et al. JANUARY 19, 2023 THE JOURNAL OF PHYSICAL CHEMISTRY C

READ 🗹

Facet-Dependent Ba Dissolution of Tetragonal BaTiO₃ Single Crystal Surfaces

Hee-Joon Chun, Seong-Chan Park, et al. JANUARY 19, 2023 THE JOURNAL OF PHYSICAL CHEMISTRY C

RFA	D	
ILL A		-

Controlling Energy Transfer in Plasma-Driven Ammonia Synthesis by Adding Helium Gas

Rusen Zhou, Patrick J. Cullen, *et al.* JANUARY 25, 2023 ACS SUSTAINABLE CHEMISTRY & ENGINEERING

READ 🗹

READ 🗹

Oblique-Incidence-Excited Localized Hot Spots in Plasmonic Particle-on-Film Nanocavities

Zulhumar Turup, Min Gao, *et al.* DECEMBER 29, 2022 THE JOURNAL OF PHYSICAL CHEMISTRY C

Get More Suggestions >