Size-Specific, Dissociative Activation of Carbon Dioxide by Cobalt Cluster Anions

Akimaro Yanagimachi,[†] Kiichirou Koyasu,^{†,‡} David Yubero Valdivielso,[§] Sandy Gewinner,^{||} Wieland Schöllkopf,^{||} André Fielicke,^{*,§} and Tatsuya Tsukuda^{*,†,‡}

[†]Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan [‡]Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8520, Japan [§]Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany ^{||}Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

ABSTRACT: The reaction of cobalt cluster anions $\operatorname{Co}_n^-(3 \le n \le 17)$ with CO_2 was studied experimentally and theoretically to explore the size-specific activation mode of CO_2 by Co_n^- . Mass spectrometric measurements revealed that the reactivity depends strongly on cluster size: the reactivity emerges abruptly at n = 7, peaks at n = 8-10, and then gradually decreases with increasing n. Infrared multiple photon dissociation spectra of $\operatorname{Co}_n\operatorname{CO}_2^-$ exhibit a single peak at $\sim 1870 \text{ cm}^{-1}$, similarly to the previously reported spectra of $\operatorname{Co}_n\operatorname{CO}^-$. Density functional theory calculations for $\operatorname{Co}_7\operatorname{CO}_2^-$ as an example revealed that the dissociative adsorption of CO_2 into CO and O is energetically more favorable than nondissociative adsorption. The infrared spectra calculated for dissociated isomers $\operatorname{Co}_7(\operatorname{CO})^-$ reproduced the experimental results, whereas those for nondissociated isomers $\operatorname{Co}_7\operatorname{CO}_2^-$ did not.



Article

pubs.acs.org/JPCC

The photoelectron spectra of Co_nCO_2^- were shifted dramatically toward higher energies relative to those of Co_n^- , suggesting electron transfer from Co_n^- to the CO and O ligands. These results indicate that the CO₂ molecule adsorbs dissociatively on Co_n^- , in sharp contrast to its nondissociative adsorption onto the Co monomer anion.

1. INTRODUCTION

Emission control of carbon dioxide (CO₂), recognized as the primary greenhouse gas, is a major challenge for realizing a sustainable society. A promising approach to this issue is the catalytic conversion of the chemically inert CO₂ molecule into useful, value-added compounds.^{1,2} For example, a $CO/CO_2/H_2$ mixture has been converted to methanol using heterogeneous copper catalysts,^{2,3} and dimethyl carbonate was obtained from CO_2 using base catalysts.³⁻⁵ In these catalytic conversions, CO_2 is activated by either dissociative or nondissociative adsorption. For example, the dissociation of CO_2 into CO and O on catalysts is involved in methanation.⁶ Three modes of nondissociative adsorption of CO_2 have been reported: (1) bidentate ligation via the C–O bond in the reduction of CO_2 to CO on (NHC)Cu(boryl);^{7,8} (2) bidentate ligation via the two O atoms⁹ in the hydrogenation of CO₂ on Ni(110);¹⁰ and (3) monodentate ligation via the C atom in the fixation of CO₂ with epoxides catalyzed by Mg-Al mixed oxides.¹¹ Molecularly adsorbed CO2 is bent because of electron transfer from the catalysts to the π^* orbital of CO₂.

Recently, to gain fundamental insight into the metal– CO_2 interactions, the structures of various anionic complexes $[M(CO_2)_n]^-$ (M = Co, Ni, Cu, Ag, and Au) have been studied by infrared (IR) spectroscopy and photoelectron spectroscopy (PES) with the help of density functional theory (DFT) calculations.^{12–19} The structural motifs of $[M(CO_2)_n]^-$ vary significantly between noble metals (Cu, Ag, Au) and open-d-

shell metals (Co, Ni). Metalloformate-like complexes [M- CO_2]⁻, in which CO_2 is bound to M via the C atom with typical energies of 0.2–0.4 eV, are formed as stable units for M = Cu, Ag, and Au.^{12–15,18} The CO₂ ligand is reductively activated by partial electron transfer from M; the excess charge on CO_2 is reduced in the order of Cu > Ag > Au, reflecting the electronegativity of the metal atom. In contrast, metalate complexes $[CO_2MCO_2]^-$ in which a metal cation M^+ is coordinated by two negatively charged CO₂ in a C-O bidentate fashion, are typically formed for M = Co, Ni.^{16,17} A red-shift of the antisymmetric vibrational mode of CO₂ in $[CO_2MCO_2]^-$ indicated a reductive activation of the CO₂ ligands. Although a theoretical calculation predicted that the dissociative addition is energetically more preferable, it is proposed that this process is hindered because of a high activation barrier.^{16,17} The nondissociative activation of CO_2 was also reported on a gas-phase Ni(I)-tetraazamacrocycle complex.²⁰

Motivated by these reports, we study here the interaction of CO_2 with metal clusters with a focus on how CO_2 is activated. The binding mode of CO_2 on metal clusters may be affected by their size-specific electronic and geometric structures. Co clusters were chosen as a target because Co-based catalysts have

```
Received:
April 29, 2016

Revised:
June 13, 2016

Published:
June 13, 2016
```

been used in syngas (H₂ and CO) production via the CO₂ reforming of methane.²¹ The size-dependence of the reactivity of Co_n⁻ to CO₂ was studied using mass spectrometry. The structures of the Co_nCO₂⁻ products were examined using infrared multiple photon dissociation spectroscopy (IRMPD), PES, and DFT calculations. The present study reveals that CO₂ is dissociatively adsorbed on Co_n⁻ but not the Co atomic anion.¹⁶

2. METHODS

2.1. Experiments. Experimental apparatuses in Tokyo and Berlin were used. The apparatus in Tokyo is composed of four parts: a laser ablation cluster source, a reaction cell, a time-offlight (TOF) mass spectrometer, and a magnetic-bottle type TOF photoelectron spectrometer.²² Before the experiment, all the stainless-steel pipes used for the carrier and reaction gases were baked at 100 °C under vacuum to remove water from their inner surfaces. The surface of the Co target rod was polished with sandpaper immediately before use. First, the second harmonic of a Nd:YAG laser (~10 mJ/pulse) was focused onto the Co rod (99.98%; $\phi = 5 \text{ mm}$) that was rotating and translating under a pulsed helium carrier gas (99.999%) to generate Co cluster anions. The Co cluster anions were introduced into a reaction cell at room temperature by passing through a channel ($\phi = 2.0$ mm; length = 25.5 mm). In the reaction cell, the clusters were allowed to react with CO₂ (>99.5 vol %). The anionic products were accelerated up to 2.00-4.25 keV in the TOF mass spectrometer with a typical mass resolution of 180 at $m/z \sim 530$. Mass spectra were acquired for 1000 laser shots at 10 Hz. Photoelectron spectra of the mass selected Co_n^- and $Co_n CO_2^-$ were recorded by irradiating the third harmonic of a Nd:YAG laser (~0.2 mJ/ pulse) by accumulating 5000-20 000 laser shots. Photoelectron spectra of Co,,⁻ were recorded after deceleration and calibrated using two peaks of the spectrum of Co_6^{-23-25} The resolution of the photoelectron spectrometer is <120 meV for electrons with a kinetic energy of 1.0 eV.

The apparatus in Berlin was used for infrared multiple photon dissociation (IRMPD) spectroscopy. The experiments were performed at the Fritz Haber Institut (FHI) in Berlin, Germany, using the FHI free electron laser (FHI FEL).^{26,27} The experimental apparatus consists of a laser ablation cluster source, a reaction channel, and a reflectron TOF mass spectrometer and is connected to the FHI FEL beamline for the IRMPD experiment. A dual target laser ablation source with two identical Co target rods was used as a cluster source. Details of this source and its operation are given elsewhere.²⁸ CO2 gas was injected into a reaction channel at room temperature to form metal cluster complexes. Next, the anionic products were analyzed using the reflectron TOF mass spectrometer. Mass-specific IRMPD spectra were recorded by irradiating the cluster beam with IR laser light from the FEL before mass separation and analyzing the intensity changes of the mass peaks of CO₂ complexes and product ions.

2.2. Theoretical Calculations. DFT calculations were conducted to obtain optimized structures of Co_7^- and $Co_7CO_2^-$ (see Section 3.3 for details). We used the B3LYP functional as well as the LANL2DZ basis set for C o and the 6-31++G(d) basis set for C and O. Frequency calculations were performed to confirm that each stationary point corresponds to a local minimum structure. The charges on Co_7 and CO_2 units were estimated by natural population analysis. A scaling factor of 0.980 was used for the calculated frequencies that gives, on

average, good agreement between the calculated frequencies for the free CO stretch and CO₂ antisymmetric stretch modes (2158 and 2362 cm⁻¹) and the experimental values (2170 and 2349 cm⁻¹), respectively. This suggests that the application of this scaling factor to the calculated frequencies of the ligands was reasonable. The obtained energies of the clusters were corrected by the vibrational zero-point energy. All calculations were performed using the Gaussian 09 package.²⁹

3. RESULTS AND DISCUSSION

3.1. Reaction of Co_n^- and CO_2. Figure 1a shows a portion of the mass spectrum of the Co cluster anions before reaction



Figure 1. Mass spectra of Co_n^- (a) before and (b) after reaction with CO_2 as obtained with the Tokyo apparatus.

with CO₂. The Co_n⁻ are found to be the dominant species. The mass peaks of oxidized species such as Co_nO⁻ and Co_nO₂⁻ were significantly suppressed by baking of the gas-supply pipes. The peak intensity of Co₅⁻ shows a magic-number behavior consistent with a previous study.^{23,24} After the reaction with CO₂ (Figure 1b), the peak intensities of Co_n⁻ decrease, and peaks assigned to Co_nCO₂⁻ appear. At a higher CO₂ concentration, Co_n(CO₂)₂⁻ was also formed.

The reaction of Co_n^- with CO_2 leads to the formation of the adduct $\text{Co}_n \text{CO}_2^-$ via eq 1

$$\operatorname{Co}_{n}^{-} + \operatorname{CO}_{2} \to \operatorname{Co}_{n} \operatorname{CO}_{2}^{-} \tag{1}$$

However, this reaction induces neither loss of Co atoms nor electron emission. The suppression of the fragmentation and electron emission can be understood from an energetics viewpoint: the bond dissociation energies of Co_{n-1} –Co (>1.45 eV for n = 3-20)^{30,31} as well as the electron affinities (>1.6 eV for $n \ge 3$)^{23–25} are larger than the adsorption energy of CO₂ on Co_n^- (<1.2 eV for n = 7, see Tables 1 and 2).

Because the concentration of CO_2 ([CO_2]) is much higher than that of Co_n^- and can be treated as a constant during the reaction, the rate constant for the reactions of Co_n^- (k_n) was estimated by assuming pseudo-first order reaction kinetics:

$$\ln\left(\frac{[\mathrm{Co}_n^-]}{[\mathrm{Co}_n^-]_0}\right) = -k_n[\mathrm{CO}_2]t \tag{2}$$

where $[Co_n^-]_0$ and $[Co_n^-]$ indicate the concentrations of Co_n^- before and after the reaction, respectively, and *t* indicates the reaction time. The concentration of Co_n^- was determined from the peak area of Co_n^- . The rate constant k_n was normalized by that of the most reactive cluster k_8 .

The Journal of Physical Chemistry C

$$\frac{k_n}{k_8} = \ln \left(\frac{\left[\operatorname{Co}_n^- \right]_0}{\left[\operatorname{Co}_n^- \right]} \frac{\left[\operatorname{Co}_8^- \right]}{\left[\operatorname{Co}_8^- \right]_0} \right)$$
(3)

Figure 2 shows the relative rate constant (k_n/k_8) as a function of the cluster size. Small Co_n⁻ clusters $(n \le 6)$ show almost no



Figure 2. Size dependence of the relative rate constant.

reactivity. The relative rate constant increases abruptly at n = 7, peaks around n = 8-10, and then decreases monotonically with increasing n. The decrease between n = 15 and 16 is greater than that between other neighboring sizes. Interestingly, the observed size dependence of the reactivity of CO₂ is similar to that found in the reactivity of CO toward Co_n^{-24,32,33}.

Notably, we discovered that Co_n^- reacts with CO_2 only when the cluster size is larger than or equal to 7. The size-specific reactivity of Co_n^- to CO has been explained in terms of an effective interaction between the molecular orbitals of CO and the d-orbitals of $\text{Co}_n^{-.32,33}$ It is also well recognized that charge transfer from the metal surface to the antibonding orbital of CO₂ induces the chemisorption of CO₂ in a bent form.^{9,34,35} These results suggest that the size-dependent reactivity observed here is related to the electronic structures of Co_n^- , although no obvious correlation with the size-dependent behavior of photoelectron spectra of Co_n^- was found.³⁶ Further study is needed to explain the size-specific reactivity of Co_n^- .

3.2. Infrared Multiple Photon Dissociation Spectroscopy of Co_nCO_2^-. To gain insight into the structures of CO_2 adsorbed on Co_n^- , IRMPD spectra of $Co_nCO_2^-$ were recorded. Figure 3a shows the IRMPD spectra of $Co_nCO_2^-$ (n = 7-13) in the range of 1000-2000 cm⁻¹. For all the sizes, a single absorption band is visible at ~1870 cm⁻¹. The band positions found for $Co_nCO_2^-$ are very similar to those of Co_nCO^- (ref 37) and show a similar, but weaker size-dependence (Figure 3b). The C-O stretching frequencies for Co_nCO^- increase with cluster size from 1860 (n = 7) to 1881 cm⁻¹ (n = 13): this trend has been explained by the effect of the cluster-sizedependent charge delocalization on the amount of π -backdonation to the CO ligand.³⁷ The strong similarities between the peak positions for $Co_nCO_2^-$ and Co_nCO^- suggest that CO_2 is dissociatively adsorbed on Co_n^- to form $Co_n(CO)O^-$.

Figure 4a shows the mass spectra of reaction products of Co_n^- and CO_2 before and after IR irradiation at ~1870 cm⁻¹. Upon IR irradiation, the intensities of the mass peaks of $Co_nCO_2^-$ decrease, while those of the mass peaks of Co_n^- increase significantly. The signal intensities of bare Co_n^- clusters are unaffected by this photoirradiation. The clear identification of a CO stretching band (Figure 3a) excludes the possibility that the dissociation of a CO₂ ligand is induced by the IR excitation, as has been observed for the N₂O ligand bound to Rh clusters.^{38,39} The IR-induced fragmentation process of $Co_nCO_2^-$ is expressed as follows:

Article



Figure 3. (a) Infrared multiple photon dissociation spectra of Co_nCO_2^- (n = 7-13). (b) The C–O stretching frequencies of Co_nCO^- (ref 37) and the peak positions for Co_nCO_2^- as a function of cluster size.

$$\operatorname{Co}_n(\operatorname{CO})\operatorname{O}^- \xrightarrow{\operatorname{IR}} \operatorname{Co}_n\operatorname{O}^- + \operatorname{CO}$$
 (4)

In this equation, the CO ligands act as a chromophore for the IR radiation. IR-induced fragmentation was analyzed in more detail by subtracting the mass spectrum taken after the IR irradiation from that before the radiation (Figure 4b). In addition to eq 4, we observed IR-induced fragmentation of larger clusters $\text{Co}_n(\text{CO}_2)_m^-$ into Co_nO_m^- (m = 2-4). This observation suggests that all the CO₂ ligands on Co_n^- are adsorbed also dissociatively into CO and O.

3.3. DFT Calculations of Co₇CO₂⁻. DFT calculations were conducted on $\mathrm{Co_7\mathrm{CO_2}^-}$ because $\mathrm{Co_7^-}$ is the smallest cluster that exhibits its activity. The purpose of this calculation is not to determine the global minimum structure but to confirm that CO_2 is dissociated on Co_n^- . It is reported that the most stable isomer of neutral Co7 has a pentagonal bipyramidal⁴⁰ or capped octahedral (spin multiplicity of 16)^{31,41} structure depending on the calculation methods used. Cationic Co7⁺ has a capped octahedral structure with a spin multiplicity of 17.42 On the basis of these reports, we only considered pentagonal bipyramidal and capped octahedral structures for Co7-. Figure 5 shows the optimized structures and their relative stabilities for spin multiplicities of 13, 15, and 17. The structures are very similar regardless of the spin multiplicity, and the most stable spin multiplicity for both structures is 15. In the calculation of $Co_7 CO_2^-$, the spin multiplicity was fixed as 15 to reduce the computational cost. In addition, we conducted geometrical optimization starting with the pentagonal bipyramid structure because the number of possible adsorption structures can be minimized due to its higher symmetry; furthermore, the energy difference with the most stable capped octahedron is only 0.05 eV.



Figure 4. (a) Mass spectra of reaction products of Co_n^- and CO_2 before (top) and after (bottom) IR irradiation at 1870 cm⁻¹. (b) Difference mass spectrum before and after IR irradiation at 1870 cm⁻¹.



Figure 5. Optimized structures of Co₇⁻.

First, structures of $Co_7(CO)O^-$ in which CO_2 is dissociated into the CO molecule and O atom on Co_7^- were studied systematically as follows. As shown in Scheme 1, the pentagonal



bipyramidal cluster provides five binding modes for the O atom and the CO molecule: μ_1 coordination on a single Co atom (**a** and **b**), μ_2 coordination between two Co atoms (**c** and **d**), and a μ_3 coordination among three Co atoms (**e**). We first surveyed the most energetically preferable binding sites of the O atom and CO molecule on Co₇⁻ individually.

For Co_7O^- , it was found that the O atom prefers adsorption onto site **e**. The adsorption energy (AE) and natural bond

orbital (NBO) charge (ΔQ) of the O atom were -4.94 eV and -1.26 e, respectively. For Co₇CO⁻, it was found that CO prefers adsorption onto site **a**. The AE and ΔQ values of the CO ligand were -1.22 eV and -0.06 e, respectively. Finally, we optimized the structures of Co₇(CO)O⁻ by changing the relative position of O on site **e** and CO on site **a**. Three structures (1-3) were obtained as local minimum structures (Table 1). The CO and O ligands are adsorbed close to each

Table 1. Optimized Structures of $Co_7(CO)O^-$ with C–O Bond Lengths (Å)

	1	2	3
Structure	1.17	1.17	1.17
AE (eV) ^a	-1.18	-0.71	-0.58
$v_{\rm CO} (\rm cm^{-1})^{\rm b}$	1931.2	1904.1	1904.1
$\Delta Q_{\rm CO}(e)^{c}$	-0.09	-0.04	-0.06
$\Delta Q_{\rm O}(e)^{\rm d}$	-1.19	-1.23	-1.21
VDE (eV) ^e	1.67	1.45	1.66

^{*a*}AE: adsorption energy of CO and O. ^{*b*} ν_{CO} : frequency of stretching of CO. ^{*c*} ΔQ_{CO} : NBO charge on CO. ^{*d*} ΔQ_{O} : NBO charge on O. ^{*e*}VDE: vertical detachment energy.

other on the pentagonal bipyramid core in the most stable structure (1). The pentagonal bipyramid motif was converted to a capped octahedron in structure 2 due to its comparable stability (Figure 5). The CO stretching frequencies of 1-3 were red-shifted with respect to that of free CO obtained at the same level of calculation (2158 cm⁻¹) and with respect to the experimentally determined value (2170 cm⁻¹) because of π -back-donation to the CO ligand.

For comparison, we also studied the structure of $Co_7CO_2^{-}$, where CO₂ is adsorbed nondissociatively. Three coordination configurations were considered for CO₂: (A) bidentate coordination via C and O atoms, (B) bidentate coordination via two O atoms, and (C) monodentate coordination via C atom. Three structures 4-6 were obtained as local minimum structures, as shown in Table 2. For all the structures, the AE values of CO_2 to Co_7^- are in the range of -0.5 to -0.6 eV. In the most stable structure 4, the C and O atoms of CO_2 are bonded to Co atoms at the vertex and periphery sites of Co₇-. The other two structures 5 and 6 have comparable stabilities. In structure 5, the C and O atoms of CO_2 are bonded to a single Co atom at the periphery site of Co_7^- . In structure 6, two O atoms of CO₂ are bonded to adjacent Co atoms at periphery sites of Co_7^- . Although the structures of the Co_7 moiety of 4-6remained similar to that of free Co_7^- , the structures of the CO_2 adsorbates in 4-6 are significantly different from that of free CO₂. First, the C–O bonds are lengthened from 1.17 Å to 1.21-1.29 Å upon adsorption onto Co₇⁻. This suggests that the C–O bonds of CO_2 are weakened upon adsorption onto Co_7^- . Second, the CO_2 adsorbates in **4–6** are bent with OCO angles of 129-138°. This structural change suggests that the CO₂ adsorbates are negatively charged, as reported on the metal surface.^{9,34,35} Actually, the NBO charges on CO_2 in 4–6 are in the range of -0.57 to -0.78 e, as shown in Table 2. These results indicate partial electron transfer from Co7- to the Table 2. Optimized Structures of $Co_7 CO_2^-$ with C–O Bond Lengths (Å) and OCO Angles (deg) within CO_2



^{*a*}CC: coordination configuration. ^{*b*}AE: adsorption energy of CO₂. ^{*c*} ν_{SS} : frequency of symmetric stretch of CO₂. ^{*d*} ν_{ASS} : frequency of antisymmetric stretch of CO₂. ^{*e*} ΔQ_{CO_2} : NBO charge on CO₂. ^{*f*}VDE: vertical detachment energy.

antibonding orbital of CO_2 and thus weakening of the C–O bonds of CO_2 .

Qualitatively, the $Co_7(CO)O^-$ structures (1–3) are more stable than the $Co_7CO_2^-$ structures (4–6). In particular, structure 1, the most stable isomer of $Co_7(CO)O^-$, is more stable than structure 4, the most stable isomer of $Co_7CO_2^-$, by 0.56 eV. This clearly shows that dissociative adsorption of CO_2 to Co_7^- is energetically more favorable. To aid the assignment of the spectra in Figure 3a, the vibrational spectra of 1–6 were calculated and are summarized in Figure 6. Structures 1–3



Figure 6. Infrared spectra in the range of $1000-2000 \text{ cm}^{-1}$ calculated for the isomer structures 1-6.

exhibit a single peak in the range of $1900-1930 \text{ cm}^{-1}$. The vibrational frequencies for the antisymmetric stretching mode of the adsorbed CO₂ of **4**-**6** were in the range of $1610-1790 \text{ cm}^{-1}$ and are significantly red-shifted with respect to the experimentally determined value for free CO₂ (2349 cm⁻¹). In addition, structures **4**-**6** exhibit the symmetric stretching mode of the CO₂ ligand in the range of $1120-1260 \text{ cm}^{-1}$ and the bending mode at ~700 cm⁻¹. The symmetric and antisymmetric stretching modes of **4**-**6** have comparable IR intensities, meaning that two peaks should be observed in the investigated range if Co₇CO₂⁻ is formed. Obviously, comparison of the IR

spectra of Co_7CO_2^- that were experimentally observed (Figure 3a) and calculated (Figure 6) excludes the presence of a dominant fraction of nondissociative adsorption of CO_2 on Co_n^- . Although the assignment of the IR spectrum (Figure 3) to a specific isomer is beyond the scope of this study, it is safe to conclude that CO_2 is dissociatively adsorbed to the Co_n^- cluster. The dissociative adsorption of CO_2 onto Co_n^- clusters ($n \ge 7$) is in sharp contrast to the nondissociative adsorption onto the Co monomer anion to form $[\text{CO}_2\text{CoCO}_2]^{-1.6}$ However, for comparison, dissociation of CO_2 by Ni cluster anions under thermal conditions had been suggested from the observation of Ni oxide clusters as products.⁴³

3.4. Photoelectron Spectroscopy of $Co_nCO_2^-$. The electronic structures of $Co_nCO_2^-$ were probed by PES using a photon energy of 3.49 eV. The black and red curves in Figure 7



Figure 7. Photoelectron spectra of Co_n^- (black lines) and Co_nCO_2^- (red lines) with n = (a) 7, (b) 8, and (c) 9.

show the photoelectron spectra of Co_n^- and $Co_nCO_2^-$, respectively (n = 7-9). The photoelectron spectra of Co_n^{-1} agree well with previously reported spectra, ²³⁻²⁵ although the energy resolution in previous studies was higher than that in the present study. The spectra of $Co_n CO_2^-$ have featureless profiles and are significantly blue-shifted as compared to those of Co_n^{-} . To gain more quantitative information on the effect of CO_2 adsorption on the electronic structure, the electron affinities (EAs) of Co_n and Co_nCO₂ were estimated from the spectral onset by linear extrapolation.^{23–25,44} Figure 7 shows that the EAs for $Co_n CO_2$ are larger by 0.2–0.4 eV than those for the corresponding Co_n. The increase in the electron binding energy upon CO₂ adsorption was supported by theoretical calculations: the VDE calculated for $Co_7(CO)O^-$ (1) (1.67 eV, Table 1) was larger than that for Co_7^- (1.42 eV) by 0.25 eV. It was demonstrated by PES that the EAs of $Co_n O$ (n = 7-9) were larger than those of Co_n by ~0.2 eV.⁴⁴ Thus, the increase of the EAs for $Co_n CO_2$ is ascribed to the electron transfer from the Co_n cluster to the O atom as evidenced by NBO analysis (Table 1). However, shifts of the EAs for $Co_{\mu}CO_{2}$ are slightly larger than those for Co.O.44 The stabilization of the frontier orbitals of Co_nO^- and CO via bonding interaction may contribute to these additional increments.³

4. CONCLUSIONS

Mass spectrometric studies showed that Co_n^- clusters of $n \ge 7$ react with CO_2 . IR spectroscopy and DFT calculations revealed that CO_2 is dissociatively adsorbed on the Co_n^- clusters, in

sharp contrast to its nondissociative adsorption on the Co atomic anions. Photoelectron spectra of Co_nCO_2^- (n = 7-9) support electron transfer from the Co clusters to the CO and O ligands. The present study demonstrates that Co_n^- is an attractive candidate for catalyzing CO₂ conversion.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: fielicke@physik.tu-berlin.de.

*E-mail: tsukuda@chem.s.u-tokyo.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Prof. Hiroyuki Yoshida (Chiba University) for fruitful suggestion for the cluster production. This research was financially supported by the Elements Strategy Initiative for Catalysis and Batteries (ESICB) and by a Grant-in-Aid for Scientific Research (No. 26248003) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan. Theoretical calculations were partly performed on the supercomputers of the Research Center for Computational Science, Okazaki, Japan.

REFERENCES

(1) Waugh, K. C. Methanol Synthesis. *Catal. Today* **1992**, *15*, 51–75. (2) Yu, K. M. K.; Curcic, I.; Gabriel, J.; Tsang, S. C. E. Recent Advances in CO_2 Capture and Utilization. *ChemSusChem* **2008**, *1*, 893–899.

(3) Fang, S.; Fujimoto, K. Direct Synthesis of Dimethyl Carbonate from Carbon Dioxide and Methanol Catalyzed by Base. *Appl. Catal., A* **1996**, *142*, L1–L3.

(4) Fujita, S.; Bhanage, B. M.; Ikushima, Y.; Arai, M. Synthesis of Dimethyl Carbonate from Carbon Dioxide and Methanol in the Presence of Methyl Iodide and Base Catalysts under Mild Conditions: Effect of Reaction Conditions and Reaction Mechanism. *Green Chem.* **2001**, *3*, 87–91.

(5) Wu, Y.; Liu, G. Organocatalyzed Cycloaddition of Carbon Dioxide to Aziridines. *Tetrahedron Lett.* **2011**, *52*, 6450–6452.

(6) Wei, W.; Jinlong, G. Methanation of Carbon Dioxide; An Overview. *Front. Chem. Sci. Eng.* **2011**, *5*, 2–10.

(7) Laitar, D. S.; Müller, P.; Sadighi, J. P. Efficient Homogeneous Catalysis in the Reduction of CO_2 to CO. J. Am. Chem. Soc. **2005**, 127, 17196–17197.

(8) Zhao, H.; Lin, Z.; Marder, T. B. Density Functional Theory Studies on the Mechanism of the Reduction of CO_2 to CO Catalyzed by Copper (I) Boryl Complexes. J. Am. Chem. Soc. **2006**, 128, 15637–15643.

(9) Freund, H.-J.; Roberts, M. W. Surface Chemistry of Carbon Dioxide. Surf. Sci. Rep. 1996, 25, 225–273.

(10) Wambach, J.; Illing, G.; Freund, H.-J. CO₂ Activation and Reaction with Hydrogen on Ni(110): Formate Formation. *Chem. Phys. Lett.* **1991**, *184*, 239–244.

(11) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. Mg-Al Mixed Oxides as Highly Active Acid-Base Catalysts for Cycloaddition of Carbon Dioxide to Epoxides. *J. Am. Chem. Soc.* **1999**, *121*, 4526–4527.

(12) Boese, A. D.; Schneider, H.; Glöß, A. N.; Weber, J. M. The Infrared Spectrum of $Au^{-\bullet}CO_2$. J. Chem. Phys. 2005, 122, 154301.

(13) Knurr, B. J.; Weber, J. M. Solvent-Driven Reductive Activation of Carbon Dioxide by Gold Anions. J. Am. Chem. Soc. 2012, 134, 18804–18808.

(14) Knurr, B. J.; Weber, J. M. Solvent-Mediated Reduction of Carbon Dioxide in Anionic Complexes with Silver Atoms. J. Phys. Chem. A 2013, 117, 10764–10771.

(15) Knurr, B. J.; Weber, J. M. Structural Diversity of Copper $-CO_2$ Complexes: Infrared Spectra and Structures of $[Cu(CO_2)_n]^-$ Clusters. *J. Phys. Chem. A* **2014**, *118*, 10246–10251.

(16) Knurr, B. J.; Weber, J. M. Infrared Spectra and Structures of Anionic Complexes of Cobalt with Carbon Dioxide Ligands. J. Phys. Chem. A 2014, 118, 4056–4062.

(17) Knurr, B. J.; Weber, J. M. Interaction of Nickel with Carbon Dioxide in $[Ni(CO_2)_n]^-$ Clusters Studied by Infrared Spectroscopy. J. Phys. Chem. A **2014**, 118, 8753–8757.

(18) Zhang, X.; Lim, E.; Kim, S. K.; Bowen, K. H. Photoelectron Spectroscopic and Computational Study of $(M-CO_2)^-$ Anions. M = Cu, Ag, Au. J. Chem. Phys. **2015**, 143, 174305.

(19) Graham, J. D.; Buytendyk, A. M.; Zhang, X.; Kim, S. K.; Bowen, K. H. Carbon Dioxide is Tightly Bound in the $[Co(Pyridine) (CO_2)]^-$ Anionic Complex. J. Chem. Phys. **2015**, 143, 184315.

(20) Menges, F. S.; Craig, S. M.; Tötsch, N.; Bloomfield, A.; Ghosh, S.; Krüger, H.-J.; Johnson, M. A. Capture of CO_2 by a Cationic Nickel(I) Complex in the Gas Phase and Characterization of the Bound, Activated CO_2 Molecule by Cryogenic Ion Vibrational Predissociation Spectroscopy. *Angew. Chem., Int. Ed.* **2016**, *55*, 1282–1285.

(21) Budiman, A. W.; Song, S.-H.; Chang, T.-S.; Shin, C.-H.; Choi, M.-J. Dry Reforming of Methane Over Cobalt Catalysts: A Literature Review of Catalyst Development. *Catal. Surv. Asia* **2012**, *16*, 183–197. (22) Watanabe, T.; Tsukuda, T. Structural Characterization of Unprecedented Al₁₄O⁻ and Al₁₅O₂⁻; Photoelectron Spectroscopy and Density Functional Calculations. *J. Phys. Chem. C* **2013**, *117*, 6664–6668.

(23) Yoshida, H.; Terasaki, A.; Kobayashi, K.; Tsukada, M.; Kondow, T. Spin-Polarized Electronic Structure of Cobalt Cluster Anions Studied by Photoelectron Spectroscopy. *J. Chem. Phys.* **1995**, *102*, 5960–5965.

(24) Yoshida, K.; Terasaki, A.; Kondow, T. Photoelectron Spectroscopy of Co_n^- and Product Anions of Co_n^- with O_2 and N_2 . Surf. Rev. Lett. **1996**, 03, 667–670.

(25) Liu, S.-R.; Zhai, H.-J.; Wang, L.-S. Electronic and Structural Evolution of Co_n Clusters (n = 1-108) by Photoelectron Spectroscopy. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2001**, *64*, 153402.

(26) Schöllkopf, W.; Gewinner, S.; Erlebach, W.; Junkes, H.; Liedke, A.; Meijer, G.; Paarmann, A.; von Helden, G.; Bluem, H.; Dowell, D.; et al. The New IR FEL Facility at the Fritz-Haber-Institut in Berlin. *Proceedings of the 36th Free Electron Laser Conference*, Basel, Switzerland, August 25–29, 2014; pp 629–634.

(27) Schöllkopf, W.; Gewinner, S.; Junkes, H.; Paarmann, A.; von Helden, G.; Bluem, H.; Todd, A. M. M. The New IR and THz FEL Facility at the Fritz Haber Institute in Berlin. In *Proceedings of SPIE Volume 9512: Advances in X-ray Free-Electron Lasers Instrumentation III*; Biedron, S. G., Ed; SPIE: Bellingham, WA, 2015, 95121L.

(28) Truong, N. X.; Haertelt, M.; Jaeger, B.; Gewinner, S.; Schöllkopf, W.; Fielicke, A.; Dopfer, O. Characterization of Neutral Boron-Silicon Clusters Using Infrared Spectroscopy: The Case of Si_6B . *Int. J. Mass Spectrom.* **2016**, 395, 1–6.

(29) 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.; et al. *Gaussian 09*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

(30) Hales, D. A.; Su, C.-X.; Lian, L.; Armentrout, P. B. Collision-Induced Dissociation of Co_n^+ (n = 2-18) with Xe: Bond Energies of Cationic and Neutral Cobalt Clusters, Dissociation Pathways, and Structures. J. Chem. Phys. **1994**, 100, 1049–1057.

(31) Datta, M. S.; Kabir, M.; Ganguly, B.; Sanyal, B.; Saha-Dasgupta, T.; Mookerjee, A. Structure, Bonding, and Magnetism of Cobalt Clusters from First-Principles Calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 014429.

(32) Kapiloff, E.; Ervin, K. M. Reactions of Cobalt Cluster Anions with Oxygen, Nitrogen, and Carbon Monoxide. *J. Phys. Chem. A* **1997**, *101*, 8460–8469.

(33) Balteanu, I.; Achatz, U.; Balaj, O. P.; Fox, B. S.; Beyer, M. K.; Bondybey, V. E. The Effect of Charge upon CO-Adsorption by Ionic Group 5 and Group 9 Transition Metal Clusters. *Int. J. Mass Spectrom.* 2003, 229, 61–65.

(34) Wang, S.-G.; Liao, X.-Y.; Cao, D.-B.; Huo, C.-F.; Li, Y.-W.; Wang, J.; Jiao, H. Factors Controlling the Interaction of CO₂ with Transition Metal Surfaces. *J. Phys. Chem. C* **2007**, *111*, 16934–16940.

(35) Ko, J.; Kim, B.-K.; Han, J. W. Density Functional Theory Study for Catalytic Activation and Dissociation of CO_2 on Bimetallic Alloy Surfaces. J. Phys. Chem. C 2016, 120, 3438–3447.

(36) Liu, S.-R.; Zhai, H.-J.; Wang, L.-S. *s-d* Hybridization and Evolution of the Electronic and Magnetic Properties in Small Co and Ni Clusters. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *65*, 113401.

(37) Fielicke, A.; von Helden, G.; Meijer, G.; Pedersen, D. B.; Simard, B.; Rayner, D. M. Size and Charge State Effects on the Binding of CO to Late Transition Metal Clusters. *J. Chem. Phys.* **2006**, *124*, 194305.

(38) Hamilton, S. M.; Hopkins, W. S.; Harding, D. J.; Walsh, T. R.; Gruene, P.; Haertelt, M.; Fielicke, A.; Meijer, G.; Mackenzie, S. R. Infrared Induced Reactivity on Surface of Isolated Size-Selected Clusters: Dissociation of N₂O on Rhodium Clusters. *J. Am. Chem. Soc.* **2010**, *132*, 1448–1449.

(39) Hamilton, S. M.; Hopkins, W. S.; Harding, D. J.; Walsh, T. R.; Haertelt, M.; Kerpal, C.; Gruene, P.; Meijer, G.; Fielicke, A.; Mackenzie, S. R. Infrared-Induced Reactivity of N_2O on Small Gas-Phase Rhodium Clusters. J. Phys. Chem. A **2011**, 115, 2489–2497.

(40) Rodríguez-López, J. L.; Aguilera-Granja, F.; Michaelian, K.; Vega, A. Structure and Magnetism of Cobalt Clusters. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *67*, 174413.

(41) Ma, Q.-M.; Xie, Z.; Wang, J.; Liu, Y.; Li, Y.-C. Structures, Stabilities and Magnetic Properties of Small Co Clusters. *Phys. Lett. A* **2006**, 358, 289–296.

(42) Gehrke, R.; Gruene, P.; Fielicke, A.; Meijer, G.; Reuter, K. Nature of Ar Bonding to Small Co_n^+ Clusters and its Effect on the Structure Determination by Far-Infrared Absorption Spectroscopy. *J. Chem. Phys.* **2009**, 130, 034306.

(43) Hintz, P. A.; Ervin, K. M. Chemisorption and Oxidation Reactions of Nickel Group Cluster Anions with N_2 , O_2 , CO_2 , and N_2O . J. Chem. Phys. **1995**, 103, 7897–7906.

(44) Pramann, A.; Koyasu, K.; Nakajima, A.; Kaya, K. Photoelectron Spectroscopy of Cobalt Oxide Cluster Anions. *J. Phys. Chem. A* **2002**, *106*, 4891–4896.