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CO₂ Activation on Ni(111) and Ni(100) Surfaces in the Presence of H₂O: An Ambient-Pressure X-ray Photoelectron Spectroscopy Study

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ABSTRACT: Nickel-based catalysts play an important role in the chemical transformation of CO₂. A fundamental understanding of the interaction between CO₂ and Ni surfaces at atomic level is necessary. In this study, the interfacial reactions of CO₂ and CO₂ + H₂O mixture on Ni(111) as well Ni(100) surfaces were investigated using ambient pressure X-ray photoelectron spectroscopy as well as theoretical calculations. The results indicate that the distributions of dissociation products are very different on the Ni(111) and Ni(100) surfaces. Carbonate, CO, and graphitic carbon formed on both Ni(111) and Ni(100) surfaces in the presence of 0.2 Torr CO₂. However, more than 90% adsorption species on the Ni(111) surface is the carbonate, whereas the Ni(100) surface is mainly covered by adsorbed CO* and graphitic carbon. The co-adsorption of H₂O weakens the influence of structure effect on the interfacial interaction between CO₂ and Ni surfaces. Furthermore, the density functional theory calculations suggest that the activation of CO₂ on Ni(111) and Ni(100) tends to follow different reaction paths, which are consistent with the experimental results.

■ INTRODUCTION

The CO₂ emission from the excessive use of fossil fuels had led to serious environmental issues, such as global warming. Catalytic reduction of CO₂ to high-value-added chemicals and fuels is one of the promising approaches for CO₂ sequestration.^{1–4} A major challenge in this field is developing low-cost transition metal catalysts, such as Ni, Co, and Cu,^{5–9} for highly selective hydrogenation and photo/electrochemical reductions.^{2,4,10,11}

Among earth-abundant catalytic materials, Ni is one of the top candidates for CO₂ reduction through methanation or methanol synthesis.^{9,12–16} In these reactions, structure sensitivity is believed to play a key role in determining the reaction mechanism and product selectivity. For CO₂ hydrogenation process, Vogt recently demonstrated that the reaction activity and pathway change markedly with particle size.¹³

Theoretical studies suggest that surface orientation affects the activation of CO₂ on Ni by altering the energetics for sequential C–O bond breakage.¹⁷ Recently, the activation of CO₂ on the model Ni catalyst surfaces, Ni(111) and Ni(110), has been investigated separately by two research groups using ambient pressure X-ray photoelectron spectroscopy (APXPS) in situ technique.^{18–20} On the compact surface, carbonate is identified as the dominating surface intermediate by Heine at room temperature.¹⁸ On the open surface,

graphitic carbon is the major surface species as shown by Roiaz and Monachino at elevated temperature at 425 K.^{19,20} However, the excessive amount of graphitic carbon on Ni(110) is still under doubt, since they may be produced by the heating filament at high temperatures.¹⁸

In this work, the structure sensitivity of CO₂ activation is systematically investigated on the Ni(111) and Ni(100) model surfaces using APXPS and density functional theory (DFT) simulations. Our APXPS results show that, even at room temperature, the Ni(100) surface is capable of breaking C–O bonds to produce graphitic carbon with about 30% surface coverage. In stark contrast, the dominant surface species is carbonate on the compact (111) surface. These observations are further corroborated by DFT calculations of the energetics of competing elementary processes. Moreover, the subsequent addition of H₂O on the Ni surfaces induces marked changes in the distribution of surface species.

■ EXPERIMENTAL SECTION

The APXPS experiments were carried out at Beamline 9.3.2 of the Advanced Light Source at Lawrence Berkeley National

Laboratory.²¹ Before the experiments, the APXPS chamber was baked at 120 °C for 48 h, achieving a base pressure of 8×10^{-10} Torr. The nickel single crystals were cleaned by several cycles of Ar⁺ sputtering (2 keV, 15 mA) and annealing at 600 °C.^{22,23} The clean Ni(111) and Ni(110) surfaces were produced, as verified by the XPS spectra and low-energy electron diffraction (LEED) (Figure S1). H₂O (research grade) was purified by repeated freeze–pump–thaw cycles.²⁴ To minimize contamination, the gas lines for CO₂ and H₂O were baked at 120 °C for 2 h and flushed several times using high-purity CO₂ (99.999%) or H₂O before introducing CO₂ or H₂O into the chamber.

Incident photon energy (E_{hv}) of 410 eV for C 1s and 650 eV for O 1s were used to produce ejected photoelectrons with kinetic energy (E_{kin}) $\sim$ 120 eV, corresponding to electron inelastic mean free path of around 0.43 nm.²⁵ Unless otherwise stated, the spectra were fitted by Casa XPS software using a Shirley-type background. The symmetrical peaks were fitted using the GL(30) line shape (a mixing of 70% Gaussian and 30% Lorentzian), whereas the asymmetric Ni 3p peaks were fitted using the DS(0.02,100)GL(30) line shape, a hybrid Doniach Sunjic/Gaussian–Lorentzian (product).²⁶ The detailed fitting procedure is given in Section IV of the Supporting Information (SI).

All DFT calculations were performed with Vienna ab initio simulation package.^{27–29} The revised Perdew–Burke–Ernzerhof (RPBE) functional was used to describe the electron–ion interaction in projector-augmented wave approach.^{30–33} Spin polarization was taken into consideration due to the magnetism of nickel, and the electron occupancy was determined using Methfessel–Paxton scheme with a smearing width of 0.1 eV.³⁴ Adsorption geometries were optimized using a force-based conjugate gradient algorithm, whereas transition states (TSs) were located with a constrained minimization method.^{35–37} The force convergence was set to 0.05 eV/Å with a total energy convergence of 10^{-4} eV and the energy cutoff for the plane-wave expansion was set to 500 eV. The Ni(111) and (100) surfaces were modeled as a periodic four-layer slab with half of the layers fixed at their bulk positions. The $p(3 \times 3)$ supercell was chosen with a $(4 \times 4 \times 1)$ Monkhorst–Pack k -point mesh for Ni(111) and $(3 \times 3 \times 1)$ for Ni(100).³⁸ A vacuum spacing of more than 15 Å was placed above the surface. The adsorption energy was calculated using the equation: $E_{\text{ad}} = E_{\text{A/S}} - E_{\text{S}} - E_{\text{A}} - E_{\text{A/S}}$ and E_{S} represent the energies of the slab with and without the adsorbate, respectively, and E_{A} represents the adsorbate energy in the gas phase. Previous research shows that the DFT calculation of the carbon–oxygen double bond has a systematic error, and the correction for RPBE is +0.41 eV for the gaseous CO₂.³⁹

RESULTS AND DISCUSSION

CO₂ Adsorption on Different Ni Single-Crystal Surfaces. To study the influence of surface orientation on the CO₂ activation, Ni(111) and Ni(100) surfaces were exposed to CO₂ in the main chamber at room temperature. Figure 1a,b show the C 1s spectra of the surfaces species on Ni(111) and Ni(100) in the presence of 0.2 Torr CO₂, respectively. The C 1s spectra exhibit three main spectral regions: (i) the peak with binding energy (BE) of 293.0 eV comes from the CO₂ gas phase; (ii) the peaks located at 288.8 and 290.0 eV are attributed to two kinds of carbonate species (“carbonate I” and “carbonate II”);^{18,40} (iii) the peaks with

Figure 1. (a, b) C 1s spectra on Ni(111) and Ni(100), respectively, and (c) and (d) the corresponding O 1s spectra. The O 1s spectrum in (d) is scaled by a factor of 2 for clarity. CO₂ adsorption was performed in 0.2 Torr CO₂ at room temperature. All of the spectra were collected with a photoelectron kinetic energy of 120 eV.

BEs of 284.8 and 285.6 eV can be assigned to the graphitic carbon and adsorbed CO (CO*), respectively.^{18,41–43}

Figure 1c,d show the O 1s spectra of the adsorption species on the Ni(111) and Ni(100) surfaces in the presence of 0.2 Torr CO₂, respectively. The peaks with BEs of 536.6 and 529.5 eV are assigned to the gas phase CO₂ and NiO, respectively.⁴⁴ The O 1s peak at 531.1 eV can be attributed to both CO* and carbonate species.^{18,20} The peaks with BEs of 532.7 and 530.8 eV are attributed to the adsorbed H₂O and hydroxy (OH).^{45,46} The presence of H₂O and OH on the Ni surfaces is due to the H₂O background pressure. The effect of H₂O on the adsorbed species will be discussed later.

Compared with that in the ultra-high vacuum (UHV) conditions, the adsorption and dissociation of CO₂ on Ni surfaces under ambient pressure conditions show a significant difference. The previous UHV studies indicate that the linear CO₂ is physisorbed on the Ni(110) and Ni(100) surfaces at 100 K, and it transforms into bent chemisorbed CO₂ (CO₂*) at 120–200 K.^{23,47,48} The CO₂* further dissociates into CO* and atomic oxygen above 200 K. In addition, only physisorbed CO₂ is formed on the Ni(111) surface below 100 K. Neither chemisorbed CO₂ nor dissociated CO₂ is observed above 120 K on this surface.⁴⁷ From Figure 1, in addition to carbonate, CO* and graphitic carbon species are found on both Ni(111) and Ni(100) surfaces in the presence of 0.2 Torr CO₂. However, there is no peak related to CO₂* (with BE of 286–287 eV), which results from the unstable state of CO₂* above 220 K.⁴⁸

Heine et al. previously reported that two carbonate species, corresponding to two C 1s peaks at 288.9 and 289.7 eV, formed on the Ni(111) surface under 0.2 Torr CO₂ at room temperature.¹⁸ In our study, we started the scan of C 1s spectra immediately after the introduction of CO₂. A peak around 288.8 eV appeared on the Ni(111) surface at the beginning (as

shown in Figure S2). A small amount of CO* and graphitic carbon appeared when the pressure was stable at 0.2 Torr (~30 min after introducing CO₂). The minor difference between our work and previous study (CO* and graphitic carbon) could be a result of the defect sites and/or steps on the Ni(111) surface (shown in Figure S1). The possible beam-induced effect was evaluated by collecting the spectra at two spots with different irradiating time. The results (Figure S3) indicated that the beam-induced effect was negligible in our experiment.

On Ni(111), two C 1s peaks with BEs at 288.8 eV (carbonate I) and 290.0 eV (carbonate II) can be identified (Figure 1a). The depth-profile XPS experiments carried out using the photoelectron kinetic energies (E_{kin}) at 120 and 360 eV (Figure S4) indicate that carbonate II is slightly surface rich. This difference is not sufficient for a clear bulk and surface assignment.¹⁸ Therefore, we assign them as two different carbonate species found on the surface. These results are consistent with previous studies.¹⁸ Figure 1b shows that the peak intensities of the carbonate species on Ni(100) are substantially weaker than those on Ni(111). However, carbonate I and carbonate II species can still be resolved in our XPS analysis.

Even though the CO₂ adsorption on Ni(110) and Ni(100) surfaces is similar under UHV conditions, our results indicate that CO₂ adsorption on Ni(100) is different from that on Ni(110) under ambient pressure conditions.⁴⁹ We find that the Ni(100) surface is covered by adsorbed CO*, graphitic carbon, and a little carbonate. However, the carbonate, two CO species, and three graphitic carbon species are observed on the Ni(110) surface in 0.01 mbar CO₂ at 425 K.¹⁹ The difference could be a result of difference in the reactivities between the Ni(110) and Ni(100) surfaces.

The significant difference in the distribution of adsorbed species on Ni(100) and Ni(111) surfaces is attributed to the fact that the dissociation of CO₂ on these two surfaces tends to follow different reaction routes. According to the peak intensities of each species from C 1s spectra (shown in Figure 1a,b), we can calculate the relative concentration of different surface carbon species. As shown in Figure S5, the major species on Ni(100) are adsorbed CO* (54%, relative content) and graphitic carbon (33%). However, the dominant species on Ni(111) is carbonate (73%), with a small amount of graphitic carbon (10%) and CO* (17%). The adsorbed CO* originates from the dissociation of CO₂ (CO₂ → CO* + O*). Then, the reaction of O* with CO₂* leads to the formation of the carbonate (O* + CO₂* → CO₃*). The graphitic carbon comes from the further dissociation of CO* (CO* → C* + O*). On both Ni(111) and Ni(100) surfaces, the first reaction step is the cleavage of the C–O bond in CO₂ (CO₂* → CO* + O*). Then, on the Ni(111) surface, the reaction between atomic oxygen and adsorbed CO₂ leads to the formation of carbonate. However, on the Ni(100) surface, the next step is the decomposition of CO* rather than the formation of carbonate.

To understand these experimental findings, we performed DFT calculations to compare the activation barriers and reaction energies of elementary steps, namely, the dissociation of CO₂ to CO* and O*, the dissociation of CO* to graphitic carbon and oxygen, and the oxidation of CO₂ to produce CO₃*, on Ni(111) and Ni(100). To see more clearly how CO₂ dissociates on the surfaces, the transition state (TS) configurations are plotted in Figure 2 and the reaction barriers

Figure 2. Structure of adsorbates and transition states on Ni(111) and Ni(100). CO₂*, CO₃*, CO*, C*, O*, and TS1 for CO₂* dissociation, TS2 for CO* dissociation, and TS3 for CO₃* formation.

are shown in Table 1. As one can see from Table 1, the adsorption of CO₂ on Ni(100) is much stronger than that on

Table 1. Reaction Barriers and Reaction Energies of Elementary Steps on Ni(111) and Ni(100) Surfaces

reactions	$E_a(111)$	$\Delta E(111)$	$E_a(100)$	$\Delta E(100)$
CO ₂ → CO ₂ *		0.11		−0.27
CO ₂ * → CO* + O*	1.34	−1.08	0.33	−1.02
CO* → C* + O*	3.15	1.42	1.96	−0.18
O* + CO ₂ * → CO ₃ *	0.65	0.40	1.05	0.29

Ni(111), and the subsequent dissociation of CO₂ is much easier on Ni(100). The difference between the activation energies of CO₂ dissociation to CO* and O* on these two surfaces is as high as 1.01 eV. Further dissociation of CO gives rise to high barriers of 3.15 and 1.96 eV on Ni(111) and Ni(100), respectively, indicating that this step is relatively slow but the barrier is also much lower on Ni(100). It is interesting to see that there is competition between the dissociation and oxidation of CO₂ on the two surfaces, and the preferred reaction pathways are different on these two surfaces studied. On Ni(111), the barrier for CO₂ dissociation is much higher than the barrier for CO₂ oxidation, whereas the dissociation of CO₂ gives rise to a much lower barrier on Ni(100), this is consistent with the results observed experimentally that the formation of carbonate is ready to take place on Ni(111), whereas the dissociation of CO₂ and CO is preferred on Ni(100).

Figure 1a shows that the total amount of carbonates is much higher than that of CO*. The formation of carbonate follows these two elemental steps: (1) CO₂* → CO* + O* and (2) O* + CO₂* → CO₃*. If all of the dissociation products stay on the Ni surface, the content of carbonate should not be higher than that of CO*. Hence, a substantial amount of CO* must be desorbed from the carbonate- and O-covered Ni(111) surface. The desorption of certain carbon-rich species with O/C < 2 is also confirmed by the calculation of the atomic ratio of O/C of the adsorption species.

The semiquantitative analysis of the species on Ni(111) and Ni(100) (as shown in Section VII of the SI) indicates that the O/C ratio of adsorption species on Ni(111) (~4.5) is higher than that of CO₂ stoichiometric ratio (2.0), which means that

O accumulation occurred on the Ni(111) surface during the reaction. CO* is the most likely desorption species, since the desorption of graphitic carbon is impossible at room temperature.

The large amount of CO desorbed at room temperature during the CO₂ activation on Ni(111) seems to contradict to the strong adsorption of CO on Ni(111). However, under 0.2 Torr, the other co-adsorbed species, oxygen and carbonate, are energetically more stable than CO*. For example, the adsorption energy of oxygen on clean Ni(111) is about 2 times higher than that of CO*.^{50,51} Therefore, the co-adsorption of these species at high pressures can significantly weaken CO adsorption.

On Ni(100), the O/C ratio of 1.9 is close to that of CO₂ molecule, indicating that the desorption of CO* is negligible on this surface. According to our DFT calculations (Table 1), surface oxygen on Ni(100) has very low reactivity with chemisorbed CO₂ to form carbonate, and the strongly adsorbed CO* can easily dissociate into stable carbon and oxygen on the surface. The lack of carbonate formation makes more surface sites available for CO* adsorption and its further dissociation.

H₂O and CO₂ Co-adsorption on Ni(111) and Ni(100) Surface. Water always plays an important role in the real catalytic reactions. Humidity change induces significant differences in both the surface species and surface chemical state of Ni. To study the effect of H₂O on CO₂-predosed Ni surfaces, 0.2 Torr H₂O was introduced into the chamber after the pressure of CO₂ was stabilized at 0.2 Torr. The C 1s and O 1s spectra of Ni(111) as well as Ni(100) under 0.2 Torr CO₂ + 0.2 Torr H₂O are shown in Figure 3.

In the O 1s spectra (Figure 3c,d), the new peak at 535.3 eV originates from the gas-phase H₂O. The intensities of peaks at 530.9 eV (hydroxyl) and 532.6 eV (adsorbed water) increase obviously, indicating that the adsorption and dissociation of

Figure 3. (a) C 1s and (c) O 1s spectra of Ni(111) and (b) C 1s and (d) O 1s spectra of Ni(100) in 0.2 Torr CO₂ + 0.2 Torr H₂O at room temperature.

H₂O occur on the Ni surfaces. The dissociation products, hydrogen and hydroxyl, further react with CO₂ and other surface species to produce formate, methoxy, and carbonate species.⁵²

In the C 1s spectra (Figure 3a,b), the new peak at 287.0 eV can be assigned to formate,⁵² one of the CO₂ hydrogenation products. The formation of methoxy species cannot be clearly resolved because its C 1s peak position (285.6 eV) is same as that of CO*. If we assume that the introduction of H₂O on the Ni surface predosed with CO₂ has a small effect on the surface concentration of graphitic carbon, the surface concentration changes of the other carbon-containing species can be estimated by using the peak intensity of graphitic carbon as a normalization constant (Figure 4). An increase of this peak

Figure 4. H₂O-induced effects on carbon-containing species on Ni(111) and Ni(100). The C 1s peak intensity of each species is normalized by the intensity of graphitic carbon on the same crystal surface under the same reaction condition.

intensity at 285.6 eV is found on both Ni(111) and Ni(100) surfaces. Since the Ni surfaces become more oxidized after dosing with water (shown in Figure S7), and CO does not adsorb on the NiO or NiCO₃ surfaces at room temperature,¹⁸ we attribute this increase of peak intensities to methoxy formation.^{24,53}

H₂O co-adsorption on the Ni surfaces has a prominent effect on carbonate species (Figure 4). On Ni(100), the surface concentration of carbonate increases dramatically. In contrast, the surface concentration of carbonate on Ni(111) decreases upon introducing H₂O. There is a shift of the carbonate peaks about 0.5 eV toward the higher binding energy on Ni(111) (Figure 3).

The reaction of metal-bound hydroxide with CO₂ to produce carbonate has been widely studied as an approach for CO₂ fixation. The study of hydroxo complexes of metal ion shows an order in the reactivity of various metals as Zn > Co >> Ni ≈ Mn > Cu ≈ 0.⁵⁴ A recent study further demonstrates that Ni–OH rapidly reacts with CO₂ to produce a carbonate species in the form of Ni–OCO₂H.⁵⁵ Therefore, this reaction should be responsible for the H₂O-induced increase of carbonate on Ni(100).

On Ni(111), there is an initial high surface concentration of carbonate before the addition of H₂O. Upon H₂O dissociation into hydrogen and OH, carbonate hydrogenation and formation are expected to compete with each other. The steady-state surface concentration of carbonate should be

determined by the initial surface concentration and the rates of carbonate hydrogenation and formation. Similar to Ni(111), a H₂O-induced decrease of carbonate concentration has been observed previously on a carbonate-covered Co surface.

After H₂O addition, formate appears in a small amount on both Ni(111) and Ni(100) (Figure 3a,b), which suggests that, unlike Cu, hydrogenation of chemisorbed CO₂^{δ-} to formate is not a favorable reaction path on the Ni surfaces.^{56,57} Methoxy can be formed by hydrogenation of formate and carbonate.⁵⁸ The amount of methoxy formed cannot be determined in this XPS study due to the peak overlap of methoxy and CO*.

Finally, our analysis of H₂O-induced effect is based on the assumption that the change in surface concentration of graphitic carbon is small enough to be neglected. We believe that this is reasonable assumption on the CO₂-predosed surfaces at room temperature.

CONCLUSIONS

In this work, CO₂ activation and subsequent H₂O-induced effects on Ni(111) and Ni(100) are studied by APXPS and DFT calculation. Our results show that the surface orientation of Ni has a profound influence on the reaction pathway for CO₂ activation. Under 0.2 Torr of CO₂ and room temperature, carbonate species are the dominant surface intermediates on Ni(111). However, on Ni(100), adsorbed CO* and graphitic carbon are the major surface species. DFT calculations unveil that CO₂* chemisorbed on Ni(111) has a low activation energy to react with surface oxygen to form carbonate, and that, on Ni(100), the sequential C–O bond cleavage of CO₂* dissociation is energetically favorable.

Formate and methoxy are resolved by APXPS after introducing 0.2 Torr of H₂O to the CO₂-dosed Ni surfaces. Prominent changes in the surface concentration of carbonate are observed on both Ni(111) and Ni(100). On Ni(100), the concentration increases significantly. However, on Ni(111), the concentration decreases. We attribute these observations to the competition between carbonate hydrogenation by hydrogen and formation through the reaction of Ni–OH and CO₂.

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Notes

The authors declare no competing financial interest.

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