Interactions of Na, O₂, CO₂ and water with MnO(100): Modeling a complex mixed oxide system for thermochemical water splitting

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ABSTRACT

A catalytic route to hydrogen production via thermochemical water splitting is highly desirable because it directly converts thermal energy into stored chemical energy in the form of hydrogen and oxygen. Recently, the Davis group at Caltech reported an innovative low-temperature (max 850°C) catalytic cycle for thermochemical water splitting based on sodium and manganese oxides (Xu, Bhawe and Davis, PNAS, 2012). The key steps are thought to be hydrogen evolution from a Na₂CO₃/MnO mixture, and oxygen evolution by thermal reduction of solids formed by Na⁺ extraction from NaMnO₂. Our work is aimed at understanding the fundamental chemical processes involved in the catalytic cycle, especially the hydrogen evolution from water. In this project, efforts are made to understand the interactions between the key components (Na, O₂, CO₂, and water) in the hydrogen evolution steps on a well-defined MnO(100) single crystal surface, utilizing x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and temperature programmed desorption (TPD).

While some of the behavior of the catalytic system is observed with the model system developed in this work, hydrogen is only produced from water in the presence of metallic sodium, in contrast to the proposal of Xu et al. that water splitting occurs from the reaction of water with a mixture of Na₂CO₃ and MnO. These differences are discussed in light of the different operating conditions for the catalytic system and the surface science model developed in this work.
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In memory of my father, Jianguo Feng

To my beloved mother, Xinmin Zhou

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Chapter 1

Introduction

1.1 Thermochemical water splitting

Although not a primary energy source, hydrogen can serve as a clean and efficient energy carrier in conversion, storage and utilization of conventional fossil fuels as well as alternative energy sources such as hydroelectric, nuclear, solar, and wind power. The proposal of a “hydrogen economy” has been promoted and reviewed by scientific researchers and government agencies [1-8]. One key component in the hydrogen economy is hydrogen production. Industrial processes have been developed using several feedstocks such as natural gas (steam reforming and pyrolysis), coal (gasification and partial oxidation), water (electrolysis and thermal splitting) and biomass (fermentation and pyrolysis) [7, 9]. Among these feedstocks, water draws great interests because it is abundant on earth and does not result in direct carbon emissions in the hydrogen production: \( \text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2 \).

Compared to water electrolysis which dates back to the eighteenth century [10], the first scientific research project involving thermochemical water splitting was initiated only several decades ago in the 1960s [11]. This process allows for the direct conversion of thermal energy into stored chemical energy, which results in a higher overall efficiency than water electrolysis for hydrogen production. For example, from nuclear heat to hydrogen, the water electrolysis process utilizing electricity generated from a nuclear reactor gives a maximum efficiency of 36% [11], while the overall efficiency of
the thermochemical water splitting process using a sulfur-iodine cycle developed by General Atomics is estimated to be about 47% [11].

The simplest thermochemical water splitting process is the direct thermal decomposition of water above 4700 K, but it is not a practical strategy for industrial manufacture. A comprehensive list of different thermochemical water splitting processes is reviewed in Ref. [11]. In general, two types of thermochemical water splitting cycles are investigated dependent of operating temperature: the low-temperature multi-step processes, and the high-temperature two-step processes.

1.1.1. Low-temperature multi-step processes

Low temperature (T < 1200 K [12]) thermochemical water splitting processes have been in development since the 1960s. Normally, more than two steps are required. The low temperature requirement allows the application of wide range of energy sources, e.g. heat generated by nuclear plants. One well-known low temperature water splitting process developed by General Atomics is the “GA process [13]”, which consists of a sulfur-iodine cycle [13-18]. The reactions can be written as [11]:

\[
\begin{align*}
H_2SO_4 & \rightarrow H_2O + SO_2 + 0.5O_2 \\
2H_2O + I_2 + SO_2 & \rightarrow H_2SO_4 + 2HI \\
2HI & \rightarrow I_2 + H_2
\end{align*}
\]

The highest temperature in this process is 1120 K [11], which is required for the decomposition of sulfuric acid. Another “UT-3 process [19]” involves a calcium-iron-bromide cycle [20, 21]. Most of these low temperature cycles involve acidic, toxic or corrosive reagents, thus generating serious issues for industrial implementation [22].
1.1.2 High-temperature two-step processes

The study of high temperature (typically over 2000 K [12]) thermochemical water splitting processes has grown rapidly in recent years due to the development of high temperature solar energy collection systems. Reviews of high-temperature solar hydrogen production can be found in Ref. [12, 23]. Only two steps are needed to close a high temperature water splitting cycle [12]:

1st step (solar): \( M_xO_y \rightarrow xM + \frac{y}{2}O_2 \)

2nd step (non-solar): \( xM + yH_2O \rightarrow M_xO_y + yH_2 \)

where M is metal and \( M_xO_y \) is a corresponding metal oxide. The highest temperature required in the process is the thermal reduction of metal oxide to a lower metal oxidation state. Redox pairs of \( Fe_3O_4/FeO \) [24-27], \( ZnO/Zn \) [28-30], \( TiO_2/TiO_x \) [31, 32], \( Mn_3O_4/MnO \) [25], \( Co_3O_4/CoO \) [25] and mixed metal oxides [33-37] have been investigated.

1.2 Innovative thermochemical water splitting cycle based on manganese oxides

Recently, the Davis group at Caltech reported a low-temperature, manganese-oxide-based, catalytic thermochemical water splitting cycle [22]. It combines the advantages of both low and high temperature thermochemical water splitting to create a novel process which consists of only non-toxic, non-corrosive reagents and operates below 850 °C (1123 K). This cycle consists of four steps as shown in Fig. 1.1.

**Step 1: Thermal treatment of the Na\(_2\)CO\(_3\)/Mn\(_3\)O\(_4\) mixture at 850 °C.** Na\(_2\)CO\(_3\) reacts with Mn\(_3\)O\(_4\) (Mn\(^{2+}\) and Mn\(^{3+}\)) at 500 - 850 °C to form NaMnO\(_2\) (Mn\(^{3+}\)), MnO (Mn\(^{2+}\)) and release CO\(_2\).
Figure 1.1 Description of the thermochemical water splitting cycle developed by Davis’ group. There are four steps that complete this cycle. Hydrogen evolution occurs from water on manganese oxides with the presence of Na$_2$CO$_3$. Complete shuttling of Na$^+$ into and out of the manganese oxides contributes to the recyclability of the Mn-based system. (Figure reproduced from Fig. 2, Ref. [22])
\[2Na_2CO_3(s) + 2Mn_3O_4(s) \rightarrow 4NaMnO_2(s) + 2CO_2(g) + 2MnO(s) + Na_2CO_3(s)\]

**Step 2: Hydrogen evolution on the Na\(_2\)CO\(_3\)/MnO mixture at 850 °C.** In the presence of water, Na\(_2\)CO\(_3\) reacts with MnO (Mn\(^{3+}\)) to form α-NaMnO\(_2\) (Mn\(^{3+}\)) and release CO\(_2\), while water splits to produce hydrogen. Na\(^+\) in Na\(_2\)CO\(_3\) is thought to enable the oxidation of Mn from 2+ to 3+ by water. This step is the key step for hydrogen evolution and draws our primary interest.

\[2MnO(s) + Na_2CO_3(s) + H_2O(g) \rightarrow H_2(g) + CO_2(g) + 2NaMnO_2(s)\]

**Step 3: Na\(^+\) extraction from α-NaMnO\(_2\) by aqueous CO\(_2\) at 80 °C.** Water intercalates into the layered α-NaMnO\(_2\) and expands the distance between MnO\(_6\) tetrahedral sheets to greatly enhance the mobility of Na\(^+\) sandwiched between the adjacent manganese oxide layers. Then CO\(_2\) is bubbled through the α-NaMnO\(_2\) aqueous suspension to extract Na\(^+\) out and forms Na\(_2\)CO\(_3\), while the proton from water occupies the position for Na\(^+\) and forms H\(^+\) birnessite (H\(_x\)MnO\(_2\)·yH\(_2\)O) (Mn\(^{3+}\)).

\[6NaMnO_2(s) + ayH_2O(l) + (3 + b)CO_2(g) \rightarrow 3Na_2CO_3(aq) + aH_xMnO_2 \cdot yH_2O(s) + bMnCO_3(s) + cMn_3O_4(s)\]

**Step 4: Oxygen evolution by thermal reduction of solids following Na\(^+\) extraction at 850 °C.** After the Na\(^+\) extraction from α-NaMnO\(_2\), the resulting H\(^+\) birnessite compound (Mn\(^{3+}\)) is less thermally stable and is reduced to the reactant Mn\(_3\)O\(_4\) (Mn\(^{2+}\) and Mn\(^{3+}\)) in step 1 by heating at 850 °C (1123 K) which closes the cycle. The temperature for the reduction of Mn from 3+ to 2+ is much lower than the temperature over 2000 K for the reduction of metal oxides in high temperature 2-step water splitting cycles.

\[aH_xMnO_2 \cdot yH_2O(s) + bMnCO_3(s) \rightarrow (2 - c)Mn_3O_4(s) + 2yH_2O(g) + bCO_2(g) + 0.5O_2(g)\]
This manganese-oxide-based thermochemical system exhibits > 90% yield for both hydrogen and oxygen evolution and shows no sign of deactivation during five cycles. Ideally, it closes the cycle without the sacrifice of any catalytic components, and none of the material is toxic or corrosive.

1.3 Objective

In this ultra-high vacuum (UHV) surface science study, the interactions of Na, O₂, CO₂ and water with MnO(100) are investigated using x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and temperature programmed desorption (TPD) in an effort to model the complex Na₂CO₃/MnO mixed oxide system reported by Xu et al. [22] for the thermochemical splitting of water, to provide insights into the fundamentals of the reaction mechanism for hydrogen evolution on Na₂CO₃/MnO.

1.4 Model surface: MnO(100)

Fig. 1.2 shows a ball model illustration of an ideal stoichiometric MnO(100) surface, with atom sizes referenced to Mn and O bonded radii [38]. Bulk MnO has a rocksalt structure which is the simplest oxide structure [39]. In the bulk, each Mn²⁺ cation is surrounded by six equidistant O²⁻ anions, while each O²⁻ anion is surrounded by six equidistant Mn²⁺ cations. The crystal structure of MnO can be considered as the insertion of two fcc lattices of Mn²⁺ and O²⁻ ions [40]. The non-polar MnO(100) surface has the lowest surface energy among all the low miller-index surfaces, and is thermodynamically stable [39]. An ideal (100) surface exposes an atomically flat plane containing equal numbers of Mn²⁺ cations and O²⁻ anions with a square periodicity (a:b = 1:1), however in practice, surface defects such as steps or missing ions cannot be avoided.
Figure 1.2 Ball model illustration of the ideal stoichiometric MnO(100) surface. Grey spheres represent O$^{2-}$ anions, and black spheres represent Mn$^{2+}$ cations. Atom sizes are referenced to Mn and O bonded radii [38]. Surface O$^{2-}$ anions on the (100) plane are marked with lighter grey color for clarity. The top picture shows the surface periodicity (a:b = 1:1) looking down the [100] surface normal. The bottom picture shows a cross-section view along the [001] direction.
The clean MnO(100) surface shows very little rumpling or reconstruction in the ultra-high vacuum environment [41, 42].

1.5 Experimental methods

All experiments were carried out in a turbo-pumped, dual-chamber, stainless steel ultra-high vacuum (UHV) system. The preparation chamber with a base pressure of 2×10^{-10} Torr is equipped with a Leybold IQE 10/35 ion gun, a set of Princeton Research Instruments reverse view LEED optics and an Inficon Quaqrnex 200 mass spectrometer for TPD. The analysis chamber with a base pressure of 1×10^{-10} Torr is equipped with a Leybold EA-11 hemispherical analyzer and a Mg Kα radiation source for XPS, and a Na evaporator with an SAES getter as the Na source.

The MnO(100) single crystal was purchased from SurfaceNet GmbH with an EPI polish. The sample was mechanically clamped onto a Ta stage that was fastened to LN₂-cooled copper electrical feedthroughs in a sample rod manipulator. The sample temperature was directly measured by a type K thermocouple attached to the back of the single crystal through a hole in the Ta stage using Aremco 569 ceramic cement. The sample can be resistively heated to 1000 K and LN₂-cooled to 125 K.

A heating rate of 2.5 K·s^{-1} was used in TPD. The low heating rate was used to avoid thermal-induced fracture of the ceramic MnO sample. In TPD spectra, the intensity of the CO, CO₂, D₂O and D₂ traces have been corrected for relative mass spectrometer sensitivity factors. CO signals have been corrected for CO₂ cracking contributions as appropriate.

Na was evaporated onto the sample from a resistively heated Na SAES getter placed approximately 30 mm away from the sample. O₂ (Matheson, 99.998%), ^{18}O₂ (Linde Specialty Gases, >97 atom% ^{18}O, 99.9%), CO₂ (Matheson, 99.999%) and ^{13}CO₂
(Sigma-Aldrich, 99 atom % $^{13}$C, < 3 atom % $^{18}$O) were used as received. D$_2$O (Sigma-Aldrich, 99.9 atom % D) was degassed by repeated freeze-pump-thaw cycles prior to use. Gases were introduced by backfilling the chamber through a variable leak valve, and the reported exposures have been corrected for an ion gauge sensitivity of 1.4 for CO$_2$ and 1.0 for O$_2$/D$_2$O [43].

XPS spectra were acquired at 60 eV pass energy for Mn, O and Na 1s which gives a Ag 3d$_{5/2}$ line width of 1.06 eV, and 200 eV pass energy for Na KLL which gives a Ag 3d$_{5/2}$ line width of 2.1 eV. All binding energies of surfaces without Na have been referenced to an O 1s binding energy of 530.1 eV for the MnO(100) substrate using an approach similar to that of Langell et al. [42]. This value was obtained with the sample at an elevated temperature of 473 K which provides sufficient conductivity to eliminate surface charging on MnO which is an insulator at room temperature. Similarly, binding energies of Na-containing surfaces such as the NaMnO$_2$-like surface have been referenced to the O 1s binding energy value obtained with the NaMnO$_2$-like surface at an elevated temperature of 473 K which is also 530.1 eV. All XPS spectra were taken at 300 K except where noted.

Reported values for XPS Na/Mn, O/Mn and O/Na ratios are determined from the integrated intensity of the O 1s, Mn 2p and Na 1s photoemission features following satellite and Shirley background [44] subtraction. All XPS ratios have been corrected by atomic sensitivity factors except where noted. The ratio of XPS atomic sensitivity factors are estimated by $\frac{S_1}{S_2} \approx \frac{\sigma_1 \lambda_1 / KE_1}{\sigma_2 \lambda_2 / KE_2}$ as described elsewhere [45, 46], where $\sigma$ is the photoionization cross section of the element core level found in published data [47], $KE$ is the kinetic energy of the photoemitted electron, and $\lambda$ is the inelastic mean free path of
the photoemitted electron estimated by a predictive formula (TPP-2M equation [48, 49]) in the NIST Electron Inelastic-Mean-Free-Path Database [50]. A detailed description of methods used to calculate the ratios of XPS atomic sensitivity factors can be found in Appendix A. All XPS spectra shown in this work have been corrected by satellite subtraction but no background corrections have been applied.

All reported LEED patterns utilize a beam energy of 90 eV, and were collected at elevated temperatures high enough to provide sufficient conductivity to avoid surface charging. For the clean surface, a temperature of 473K was used. For Na covered surfaces, a temperature of 350 K is sufficient to prevent charging, with no thermally-induced chemical change in the deposited Na as verified by XPS.

A clean and nearly-stoichiometric MnO(100) surface was prepared by ion bombardment at room temperature (Ar⁺ bombardment, 2 KeV) and annealing to 1000 K in UHV for experiments in the absence of Na. If Na is involved, ion bombardment at elevated temperature (Ar⁺ bombardment, 2 KeV, 1000 K) and annealing to 1000 K in UHV is performed. For the cleaning procedure, ion bombardment was begun with the sample at 300 K, the temperature was raised to 1000 K in the ion beam, and then the sample was cooled back to 300 K in the ion beam before the annealing process. We note that after multiple Na doses, it was found that low temperature (300 K) ion bombardment could produce a Na-free disordered MnO(100) surface (as determined by XPS), but subsequent 1000 K annealing in UHV to order the surface always resulted in a detectable amount of Na in the surface region due to the outward diffusion of Na from the bulk at high temperatures, thereby necessitating the need for ion bombardment at elevated temperatures in the sample preparation process. After the preparation procedure, the
sample exhibits a sharp (1×1) LEED pattern (Fig. 1.3a) characteristic of a simple
termination of the rocksalt-structured (cubic) MnO bulk. This surface gives a Mn 2p$_{3/2}$
binding energy of 641.0 eV, with a satellite feature at 6.2 eV higher binding energy (Fig.
1.3b). Both values are in good agreement with previous reports for a clean and
stoichiometric MnO(100) surface [42]. A Mn 3s splitting of 6.1 eV is observed in Fig.
1.3(b), which also agrees with values reported for MnO [51-57]. XPS gives an
uncorrected O 1s to Mn 2p intensity ratio of 0.24, which matches the value for a clean
and stoichiometric MnO(100) surface reported by Langell et al. [42].
Figure 1.3 Characterizations of a clean and nearly-stoichiometric MnO(100) surface: (a) LEED pattern; (b) Mn 2p$^{3/2}$ and Mn 3s XPS spectra. Symbol S represents the shake-up satellite feature of Mn 2p$^{3/2}$. 
Chapter 2

Na Deposition on MnO(100)

2.1 Introduction

In the reported thermochemical water splitting cycle, the shuttling of Na$^+$ into and out of manganese oxides was determined to be a key factor to drive the water splitting cycle below 1000 °C. These observations provide a motivation for studying the interaction of Na with manganese oxide surfaces and any corresponding solid state reactions.

Alkali-metal-promoted, rocksalt-structured metal oxides have found applications in heterogeneous catalysis for chemistry such as the oxidative coupling of methane [58-62], oxidative dehydrogenation of ethane [61, 63], DeSO$_x$ [64-66], water gas shift [67] and soot combustion [68]. Studies of interactions between alkali metals and rocksalt-structured metal oxides are essential to understand the fundamental properties of these alkali metal-promoted catalytic surfaces. From a surface science perspective, a number of alkali metal/rocksalt-structured metal oxide surface combinations have been investigated, such as Na on NiO(111) [69], Na/K on NiO(100) [70-72], Li/Na/K on Ni(110)-O [73-75], Na/K/Cs on MgO(100) [76-81], Na on MgO(111) [77], and Na on CaO(100) [64, 66]. To the best of our knowledge, no study of interactions between alkali metals and the rocksalt-structured MnO has been reported.

In this chapter, Na deposition on MnO(100) was studied for various Na coverages. Temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS)
were used to characterize the forms of deposited Na, and CO$_2$ TPD was used as a probe to further distinguish different forms of surface Na. Low energy electron diffraction (LEED) was also used to monitor variations of the surface periodicity. A Stranski-Krastanov (SK) growth mechanism for Na deposition on MnO(100) is proposed.

2.2 Computational Methods

DFT has been used to examine the preferred adsorption site for Na on MnO(100). All calculations were performed using the projector-augmented-wave method [82, 83] within the Vienna Ab-initio Simulation Package (VASP) [84-86]. The Perdue-Burke-Errnzerhof (PBE) approximation was used to treat exchange and correlation utilizing a standard generalized gradient approximation (GGA) [87]. A 256 atom cell was used that exposed a (4×4) surface mesh with a thickness of four atomic layers along [100]. Following optimization of the bulk structure, a 15 Å vacuum gap was introduced, and the atoms in the bottom atomic layer were fixed at the bulk positions. A 1×3×3 k-point sampling based on the Monkhorst-Pack scheme [88] was used. For all calculations, the initial magnetic moments of the Mn$^{2+}$ cations ($d^5$) were set following the known AFM-II antiferromagnetic ordering in MnO [89], which is also found to be the ground-state magnetic ordering for DFT within the GGA [90]. A 400 eV cut-off energy was used throughout. For all geometry optimized structures, the forces on the individual atoms are less than 0.01 eV/Å.

In addition to PBE, PBE+U in the form proposed by Dudarev et al. [91] has been used to examine the Na adsorption site. Following the work of Franchini et al. [92] for bulk MnO and Bayer et al. [93] for MnO(100), we used a value of $U-J=6.0$ eV that is thought to be optimal for MnO.
2.3 Results and Discussion

2.3.1. Na TPD

Na TPD was used to characterize energetically-different bound forms of Na on MnO(100). Before each Na deposition, a clean and nearly-stoichiometric MnO(100) surface was prepared. The surface then was exposed to Na vapor at a sample temperature of 300 K, and TPD was run for the temperature range from 300 K to 1000 K.

Fig. 2.1 shows the TPD traces of Na (m/z = 23) from MnO(100) with increasing Na deposition time and coverage. (The method used to determine Na coverage is given in Fig. 2.2 and described in Section 2.3.2.1) For Na deposition times up to 60 seconds (1 ML), no Na desorption feature is observed. No other Na-related products such as Na$_2$O (m/z = 62), NaOH (m/z = 40) or Na-O fragments (m/z = 39) are detected. These results indicate that for coverages up to 1 ML, Na is irreversibly adsorbed. For a Na deposition time of 90 seconds (1.09 ML), a single Na desorption feature appears in the temperature range from 385 to 430 K, indicating that a second form of Na with weaker binding to the surface is present for coverages exceeding 1 ML. For increasing Na deposition times, this feature grows with a common leading edge, but shifts to higher peak temperatures with increasing coverage, suggesting a zeroth-order desorption process [94]. The activation energy of this zeroth-order desorption is estimated by an Arrhenius analysis of the leading edge data [94] as 116 kJ·mol$^{-1}$, which is close to the heat of sublimation of metallic Na (108 kJ·mol$^{-1}$) [40]. Similarly, a Na desorption feature near 400 K was reported for the desorption of a metallic Na multilayer from Au(111) [95]. In summary, two forms of Na are indicated: (1) irreversibly-adsorbed Na for coverages up to 1 ML, and (2) metallic Na above 1 ML coverage which desorbs near 430 K.
Figure 2.1 TPD traces of Na (m/z = 23) following Na deposition on the clean and nearly-stoichiometric MnO(100) surface with increasing Na deposition time (coverage). The coverage calibration is discussed in Section 2.3.2.1. Na is irreversibly-adsorbed up to 1 ML coverage, and metallic Na desorbs below 500 K above 1 ML coverage.
2.3.2. XPS study of Na deposition on MnO(100)

2.3.2.1. Na Growth Mode

Fig. 2.2 shows a plot of the Na 1s/Mn 2p XPS intensity ratio as a function of Na deposition time. The Na/Mn ratio increases linearly with increasing Na deposition time until a break point is observed for a Na dosing time of about 60 seconds. For Na exposures beyond 60 seconds, the Na/Mn ratio increases linearly, but with a lower slope. This growth behavior matches the Stranski-Krastanov (SK) growth mode [96], which can be described as the completion of a Na monolayer followed by island formation. A similar growth mode was reported for Na adsorption on MgO(111) [77] and K adsorption on NiO(100) [71]. Following the SK growth mode description, 1 ML Na coverage occurs at the break point near 60 seconds of Na exposure (Na/Mn = 0.64). Applying a linear correlation between the Na/Mn XPS intensity ratio and the break point associated with 1 ML gives the ML coverage scale on the right hand side of Fig. 2.2.

2.3.2.2. XPS spectra of deposited Na

XPS was used to characterize the Na chemical states arising from Na deposition on MnO(100). Before each Na deposition, a clean and nearly-stoichiometric MnO(100) surface was prepared. The surface was maintained at 300 K during Na deposition, and XPS spectra were collected at 300 K after deposition.

Fig. 2.3 shows the Na 1s and Na KLL XPS spectra for Na on MnO(100) at various coverages. No Na signal is detected for the clean MnO(100) surface. In the Na 1s XPS spectra, a Na 1s peak appears at 1072.2 eV for a 0.36 ML Na coverage. For Na
Figure 2.2 Na1s/Mn2p XPS intensity ratio (left ordinate) and Na coverage (right ordinate) as a function of Na deposition time. 1 ML Na coverage occurs at the break point near 60 seconds of Na exposure following the Stranski-Krastanov (SK) growth mode description.
Figure 2.3 Na 1s and Na KLL XPS spectra of Na on MnO(100) at various coverages. An oxidic Na compound is formed up to 1 ML coverage, and metallic Na builds up for coverages above 1 ML.
coverages up to 1 ML, the Na 1s binding energy remains fairly constant, indicating that Na chemical state is nominally constant within the first monolayer. For higher Na coverages above 1 ML, the Na 1s binding energy shifts to lower values. At 2.33 ML Na coverage, the Na 1s binding energy has shifted down by 0.7 eV to 1071.5 eV. At this point, two plasmon loss features are apparent at binding energies 5.7 eV and 11.4 eV higher than that of Na 1s, indicating the presence of metallic Na [69, 77, 97, 98]. The variation of the Na 1s binding energy with increasing Na coverage is highlighted in Fig. 2.4. Compared to the 1s binding energy of metallic Na, the 0.7 eV higher binding energy in the first monolayer matches the difference between Na$_2$O and metallic Na [64, 77, 98], suggesting that the Na in the first monolayer interacts strongly with the MnO substrate, resulting in the formation of an oxidic Na compound. Similar observations have been reported for Na deposition on several other rocksalt-structured metal oxides, such as MgO(111) [77] and CaO(100) [64, 66]. For MgO and CaO, the formation of Na$_2$O within the first monolayer [64, 70, 77], followed by the buildup of metallic Na [64, 76, 77] was suggested. These reports are in agreement with our results for Na on MnO(100).

A more significant variation with increasing Na coverage is observed in the Na KLL Auger features in Fig. 2.3. At 0.36 ML Na coverage, a single Na KLL peak at 263.9 eV is present, suggesting the formation of a Na surface compound [69, 97-99]. For increasing Na coverages up to 1 ML, this feature broadens. At 1 ML coverage, this signal shows evidence of a split into two separate features. A third feature at lower binding energy becomes apparent at 1.11 ML coverage, and all three features continue to grow for higher Na coverages. At 2.33 ML Na coverage, three peaks are well resolved: the Na KLL at 259.5 eV, and two plasmon loss features at binding energies 5.7 eV and
Figure 2.4 Na 1s binding energy as a function of Na coverage.
11.4 eV higher than that of Na KLL which are characteristic of metallic Na [69, 97, 98]. Compared to the KLL binding energy of metallic Na, the 4.4 eV increase for the Na compound matches the reported 4.5 eV difference of Na KLL binding energy between Na₂O and metallic Na [98], suggesting again the formation of an oxidic Na compound within the first monolayer. These results are consistent with the Na 1s results described above, and the Na KLL features appear to give a more sensitive indication of the appearance of metallic Na characterized by intense plasmon loss features. In summary, two Na chemical states are present during Na adsorption on MnO(100): oxidic Na within the first ML, and metallic Na at higher coverages.

The Na XPS and Na TPD results support the previously proposed SK growth mode of Na adsorption on MnO(100). For Na coverages up to 1 ML, Na interacts strongly with the MnO substrate to form an irreversibly-adsorbed, oxidic Na compound, followed by the formation of metallic Na islands for coverages above 1 ML.

2.3.2.3. XPS Spectra of Mn and O

Mn and O XPS signals were also examined in an attempt to probe Na binding site preferences on MnO(100). Mn and O XPS spectra were acquired in the same measurements along with the Na XPS spectra discussed above.

Fig. 2.5 shows the Mn 2p₃/₂, Mn 3s and O 1s XPS spectra of Na on MnO(100) for various Na coverages. With increasing Na coverage, both Mn 2p₃/₂ and Mn 3s signal intensities decrease due to the deposition of Na. However, no obvious differences are observed in other characteristics of the XPS signals such as peak width (FWHM), giving no indication of a change in Mn chemical state. For the rocksalt-structured metal oxide NiO, there are several reports of the partial reduction of Ni²⁺ cations to Ni⁰ metal upon
Figure 2.5 Mn 2p\textsubscript{3/2}, Mn 3s and O 1s XPS spectra of Na on MnO(100) at various coverages. No clear indication of Na binding preference to the MnO substrate is observed. Symbol S represents the shake-up satellite feature for Mn 2p\textsubscript{3/2}. 
interactions with alkali metals (Li [74, 75], Na [69, 74, 75] and K [72-75]), although similar reductions are not reported for Na on MgO(100) [77] or CaO(100) [64, 66]. In this chapter, Mn$^{2+}$ reduction to Mn$^0$ is not observed. Similar to the observations for Mn, the O 1s features also exhibit attenuated intensities with increasing Na coverage but are essentially unchanged in width and position relative to the O 1s signal from the clean surface. Hence, the XPS results for Mn and O provide no clear indication of the preferred Na binding sites on the MnO substrate. Nonetheless, the Na 1s binding energy for sub-monolayer coverages of Na (section 2.3.2.2) indicates the involvement of surface O atoms to form an oxidic Na surface compound.

2.3.2.4. XPS Spectra of thermally-treated Na

Na XPS was used to investigate thermally-induced changes in deposited Na. Two surfaces were prepared for this study: surface (a) with an initial 0.36 ML Na coverage associated with irreversibly-adsorbed, oxidic Na, and surface (b) with an initial 1.26 ML Na coverage exhibiting both irreversibly-adsorbed and metallic Na. For each surface, Na XPS measurements were performed after Na deposition at 300 K, after heating to 500 K (above the temperature where Na desorption is observed in TPD), and after heating to 1000 K.

Fig. 2.6(a) shows the Na 1s and Na KLL XPS spectra for surface (a) with an initial 0.36 ML Na coverage associated with irreversibly-adsorbed Na. After heating to 500 K, Na 1s binding energy remains nominally unchanged, suggesting no change in Na chemical state. While, the Na 1s peak is sharper after heating, the peak areas are nominally constant, indicating some minor nonuniformity in the Na deposited at 300 K.
Figure 2.6 Na 1s and Na KLL XPS spectra of Na on MnO(100) for initial coverages of (a) 0.36 ML (exhibiting only irreversibly-adsorbed, oxidic Na in the first monolayer) and (b) 1.26 ML (exhibiting both irreversibly-adsorbed and metallic Na) at 300 K, after heating to 500 K, and heating to 1000 K. Symbol p represents plasmon loss features for metallic Na.
This difference shows up as a small shoulder on the higher binding energy side for the as-deposited Na. Similarly the Na KLL feature also appears sharper after heating to 500 K. These results are consistent with the Na TPD and Na XPS results, indicating that the surface concentration of Na in the first monolayer does not change for heating to temperatures up to 500 K. After further heating to 1000 K, there is a significant decrease of the Na signal intensities compared to those after heating to 500 K. Given that Na desorption is not observed in TPD above 500 K, the results indicate that irreversibly-adsorbed Na in the first monolayer diffuses into the MnO bulk and near-surface region at temperatures between 500 and 1000 K.

Fig. 2.6(b) shows the Na 1s and Na KLL XPS spectra for surface (b) with an initial 1.26 ML Na coverage exhibiting both irreversibly-adsorbed and metallic Na. After Na deposition, metallic Na is present with characteristic plasmon loss features in both Na 1s and Na KLL spectra. After heating to 500 K, the plasmon loss features characteristic of metallic Na disappear, indicating that metallic Na is no long present. This result coincides with the temperature range where the Na TPD desorption feature at 430 K is observed, leading to the conclusion that the Na desorption feature at 430 K in TPD is associated with metallic Na sublimation. XPS signals of the irreversibly-adsorbed Na remaining after heating to 500 K attenuate after heating to 1000 K, also suggesting that Na in the first monolayer diffuses into the MnO subsurface and bulk, similar to the observations for surface (a).

2.3.3. LEED study of Na adsorption on MnO(100)

LEED was used to characterize surface periodicity of clean and Na-covered MnO(100). Four surfaces were prepared: (a) the clean and nearly-stoichiometric
MnO(100) surface; (b) a surface with 1.26 ML Na coverage exhibiting both irreversibly-adsorbed and metallic Na as in Fig. 2.6b; (c) the surface in (b) heated to 500 K and exhibiting only irreversibly-adsorbed Na in the first monolayer with no metallic Na; and (d) the surface in (c) heated to 1000 K where irreversibly-adsorbed Na has diffused into the near surface region and MnO bulk. As shown in Fig. 2.7, surface (b) with both irreversibly-adsorbed and metallic Na exhibits a more diffuse (1×1) LEED pattern compared to the sharper (1×1) pattern of the clean surface (a), suggesting some disorder in the Na overlayers. Surface (c) exhibiting only irreversibly-adsorbed Na with no metallic Na also exhibits a diffuse (1×1) LEED pattern similar to surface (b), again suggesting some disorder in the Na distributed within the first monolayer. The surface in Fig. 2.6d exhibits a (2×2) LEED pattern after heating to 1000 K, indicating a surface reconstruction is associated with the inward diffusion of Na to subsurface sites at temperatures between 500 and 1000 K.

We note that our LEED observations differ from others in the literature. Langell and Cameron [100] reported a preparation procedure where 2 Kev Ar$^+$ bombardment followed by annealing at 650 K in 5×10$^{-7}$ Torr of O$_2$ was used to give a reproducible surface composition and a (1×1) LEED periodicity. Extended thermal annealing in UHV at 800 K gave rise to a (2×2) surface reconstruction, with a (6×6) periodicity obtained by heating to 1000 K. They note that varying levels of Ca segregate to their surface during annealing, and that the amount of Ca contamination can impact the temperatures required to drive the reconstructions. We have repeated their preparation procedures (2 Kev Ar$^+$ bombardment, annealing in O$_2$, followed by prolonged UHV annealing) and fail to see any reconstructions when our XPS characterization suggests a clean near-surface
Figure 2.7 LEED patterns of (a) the clean and nearly-stoichiometric MnO(100) surface; (b) the MnO(100) surface with 1.26 ML Na coverage exhibiting both irreversibly-adsorbed, oxidic Na in the first monolayer and metallic Na; (c) the MnO(100) surface with initial 1.26 ML Na coverage heating to 500 K to remove metallic Na, and exhibiting only irreversibly-adsorbed, oxidic Na in the first monolayer; (d) the MnO(100) surface with initial 1.26 ML Na coverage heating to 1000 K, where irreversibly-adsorbed Na has diffused into the MnO subsurface and bulk.
composition. We only observe a (2×2) reconstruction in the presence of Na in subsurface sites. We feel it is likely that the Ca contamination in their study played a similar role to the Na in our study, with the Ca contamination being responsible for the observed reconstructions.

2.3.4. DFT simulation of surface Na

DFT was used to simulate the binding of Na at low coverage for insight into the preferred binding site on flat MnO(100). For both the PBE and the PBE+U simulations, the low energy binding site is found to be associated with a surface O anion, in agreement with the XPS results which suggests an oxidic character to the Na atoms within the first monolayer. Fig. 2.8 shows the predicted structures for one Na atom. While both methods predict an O anion binding sites, the binding geometry varies greatly. Fig 2.8 (a) and (b) show the local geometry of the adsorption site for PBE and PBE+U, respectively, while the impact of Na on the underlying surface layer is illustrated in Fig. 2.8 (c) and (d) for PBE and PBE+U, respectively.

For the PBE calculations, a single Na atom drives a (2×2) reconstruction of the top atomic layer of MnO(100) across the full (4×4) surface mesh. This reconstruction is not observed with DFT+U, and simple atop configuration is found for Na with a Na–O bond length of 2.32 Å. Note that while experimentally a (2×2) reconstruction was observed with LEED for Na in subsurface sites, irreversibly adsorbed Na in the first monolayer exhibits a (1×1) periodicity. For this system, PBE+U gives a structural prediction more in line with experiment.
Figure 2.8 DFT binding sites for a single Na atom on a (4x4) unit cell of MnO(100). The top figures show the predicted local binding configurations for (a) PBE and (b) PBE+U, while the bottom figures show the predicted impact of the Na atom on the underlying first atomic layer of MnO(100) for (c) PBE and (d) PBE+U. See text for description.
2.3.5. CO$_2$ TPD

CO$_2$ was used as a probe molecule to further distinguish the different forms of surface Na. Fig. 2.9 shows the TPD traces of $^{13}$CO$_2$ ($m/z = 45$) for several different surface treatments. For each TPD trace, the surface was cooled to 125 K, then exposed to 0.5 L (1 L = 1×10$^{-6}$ Torr·s) of $^{13}$CO$_2$ for TPD. For clean MnO(100) in Fig. 2.9(a), $^{13}$CO$_2$ desorbs primarily below 200 K with a peak at 150 K and a minor broad desorption feature in the range of 200 – 400 K, suggesting that CO$_2$ interacts relatively weakly with MnO(100) in the absence of Na. In Fig. 2.9(b) on the surface with a 2.33 ML Na coverage dominated by metallic Na, a high temperature $^{13}$CO$_2$ desorption feature at 735 K is observed, indicating that CO$_2$ interacts much more strongly with this surface than the clean MnO(100) due to a strong binding with metallic Na. A broad $^{13}$CO signal is also observed between 450 K and 800 K indicating a disproportionation reaction of strongly adsorbed CO$_2$ on metallic sodium [101]: $2$NaCO$_2$ → Na$_2$CO$_3$ + CO. Less than 20% of the adsorbed CO$_2$ is estimated to go through the disproportionation reaction to form Na$_2$CO$_3$, indicating that the majority of the $^{13}$CO$_2$ desorption feature originates from chemisorbed CO$_2$ on Na. In Fig. 2.9(c), a surface exposing only irreversibly adsorbed Na gives a $^{13}$CO$_2$ desorption feature at 650 K with no $^{13}$CO desorption, indicating that CO$_2$ also interacts strongly with oxidic Na in the first monolayer, but more weakly than with metallic Na. The different binding strengths of CO$_2$ clearly distinguishes the two different forms of Na. Heating a surface similar to that in Fig. 2.9(c) briefly to 600 K gives rise to the trace in Fig. 2.9(d). The 650 K CO$_2$ desorption feature at 650 K is significantly attenuated, indicating that a temperature of 600 K is sufficient to activate the thermally-induced diffusion of a significant fraction of the Na into the subsurface.
Figure 2.9 TPD traces of $^{13}$CO$_2$ (m/z = 45) following 0.5 L $^{13}$CO$_2$ adsorption on: (a) the clean and nearly-stoichiometric MnO(100) surface; (b) the MnO(100) surface with 2.33 ML Na coverage dominated by metallic Na; (c) the MnO(100) surface with an initial 1.26 ML Na coverage heated briefly to 500 K to remove metallic Na, and exhibiting only irreversibly-adsorbed, oxidic Na in the first monolayer; (d) the MnO(100) surface with an initial 1.26 ML Na coverage heated briefly to 600 K; (e) the MnO(100) surface with an initial 1.26 ML Na coverage heated to 600 K for 10 min; (f) the MnO(100) surface with an initial 1.26 ML Na coverage heated briefly to 1000 K.
Holding the temperature at 600 K for 10 minutes (Fig. 2.9e) is sufficient to drive the majority of Na in the first monolayer into the subsurface where it is no longer accessible to the CO$_2$ adsorbent. Heating to 1000 K (Fig. 2.9f), results in a CO$_2$ TPD trace similar to that from the clean surface, indicating that the remaining Na observed in XPS following similar treatments has all been driven subsurface.

2.4 Conclusion

Na adsorption on the MnO(100) surface follows the Stranski-Krastanov (SK) growth mode with two forms of Na identified. Up to 1 ML Na coverage, Na is randomly distributed on the MnO(100) surface before the completion of the monolayer and interacts strongly with the MnO substrate, binding in an oxidic form. This form of Na is irreversibly-adsorbed and diffuses into the MnO bulk at elevated temperatures above 500 K. For Na coverages above 1 ML, metallic Na islands nucleate and grow on top of the Na monolayer. Metallic Na desorbs from the surface at 430 K.
Chapter 3

CO\textsubscript{2} and Water Adsorption on MnO(100)

3.1 Introduction

In the reported thermochemical water splitting cycle, both CO\textsubscript{2} and water play important roles at various steps in the catalytic cycle. At the hydrogen evolution steps, water reacts with Na\textsubscript{2}CO\textsubscript{3}/MnO to produce hydrogen and release CO\textsubscript{2}, while Na\textsuperscript{+} intercalate into MnO\textsubscript{6} octahedral layers. In the catalyst regeneration steps, aqueous CO\textsubscript{2} extracts Na\textsuperscript{+} from MnO\textsubscript{6} layers and consequently lowers the thermal reduction temperature for recovery. Therefore, a study of interactions between CO\textsubscript{2}, water and rocksalt-structured MnO serves as the first essential step to understand the reaction mechanisms of this innovative water splitting cycle.

Comprehensive reviews of CO\textsubscript{2} chemistry on metal oxide surfaces can be found elsewhere [39, 102]. No studies have been reported of the interaction of CO\textsubscript{2} with MnO single crystal surfaces. However, CO\textsubscript{2} on other rocksalt-structured metal oxide single crystal surfaces, such as CaO(100) [103, 104] and MgO(100) [77, 103, 105-110], have been more extensively investigated. CO\textsubscript{2} interacts strongly with CaO on both defective and non-defective sites [102] to form CaCO\textsubscript{3} [102-104], but interacts more weakly with MgO and only forms carbonates on surface defect sites [103, 109, 110].

The interaction between water and metal oxide surfaces has been reviewed elsewhere [39, 111, 112]. Studies of water adsorption on rocksalt-structured metal oxide single crystal or single-crystal-supported thin film surfaces have focused primarily on
MgO(100) [113-120] and NiO(100) [121-125]. A common finding is that at room temperature in vacuum no water uptake is observed on perfect surfaces, while dissociative adsorption of water is observed in the presence of surface defects. Similar to CO\textsubscript{2}, water on ordered MnO surfaces has received less attention. Kendelewicz et al. [126] studied water adsorption on MnO(100) at room temperature by synchrotron-based XPS. It was observed that for water pressures lower than 10\textsuperscript{-4} Torr, water dissociates only on surface defects, while for higher pressures hydroxylation occurs on terrace sites.

Few results have been published for the interaction of co-adsorbed CO\textsubscript{2} and water on metal oxide single crystal surfaces [127]. A precursor-mediated interaction between water and CO\textsubscript{2} to form a H\textsubscript{2}O-CO\textsubscript{2} complex has been reported by Henderson for TiO\textsubscript{2}(110), and results in the formation of bicarbonate [127]. In this chapter, these interactions have been investigated for MnO(100) using temperature programmed desorption (TPD) and preliminary density functional theory (DFT) calculations.

3.2 Results and Discussion

3.2.1. CO\textsubscript{2} TPD

CO\textsubscript{2} TPD was used to characterize energetically-different bound forms of CO\textsubscript{2} on MnO(100). Fig. 3.1 shows the TPD traces of $^{13}$CO\textsubscript{2} (m/z = 45) on MnO(100) with increasing $^{13}$CO\textsubscript{2} coverage. For each TPD trace, the surface was cooled to 125 K, then exposed to $^{13}$CO\textsubscript{2} for TPD. Two distinguishing $^{13}$CO\textsubscript{2} desorption features are observed. At the lowest dose investigated at 0.02 L (1 L $= 1\times10^{-6}$ Torr·s), a broad $^{13}$CO\textsubscript{2} desorption feature is observed in the temperature range from 200 to 500 K with a peak maximum at 280 K. This feature grows and shifts to lower peak temperature with increasing coverage,
Figure 3.1 TPD traces of $^{13}\text{CO}_2$ (m/z = 45) following $^{13}\text{CO}_2$ adsorption with dose size from 0.02 - 0.5 L on the clean and nearly-stoichiometric MnO(100) surface.
and saturates for an exposure of 0.3 L with a peak maximum at 245 K. The apparent first-order activation energy for desorption is in the range of 15.1 - 17.4 kcal·mol⁻¹ estimated by Redhead analysis assuming a normal pre-exponential factor of 10¹³ s⁻¹ [128].

At 0.05 L of ^13^CO₂ exposure, a lower temperature ^13^CO₂ desorption feature appears with a peak maximum at 150 K. This feature continues to increase with increasing dose, then saturates for doses approaching 2 L. This apparent first-order desorption gives an activation energy of 9.1 kcal·mol⁻¹ for a pre-exponential factor of 10¹³ s⁻¹. The desorption feature from 200 K to 500 K with a peak maximum at 245 - 280 K is assigned to CO₂ adsorption on surface defects, and the desorption feature with a peak maximum at 150 K is assigned to CO₂ on terraces. Similar CO₂ desorption features are reported on other rocksalt-structured metal oxide surfaces, such as MgO(100) [77, 105, 110] and CaO(100) [104]. On MgO(100), CO₂ desorbs from terraces below 180 K and surface defects at 200 - 473 K, while on CaO(100) CO₂ desorbs from terraces below 200 K and surface defects at 200 - 500 K. These results are in good agreement with our observations. On MgO(100) CO and O₂ desorption were also observed in the same temperature range of CO₂ desorption from surface defects, suggesting the decomposition of chemisorbed CO₂ to CO and O₂ [110], while on CaO(100), a CO signal was detected suggesting the decomposition of chemisorbed CO₂ to CO and lattice oxygen [104]. However, in this chapter no ^13^CO or O₂ are observed as reaction products, indicating that ^13^CO₂ adsorbs molecularly on MnO(100).

A plot of the ^13^CO₂ TPD peak area as a function of exposure is shown in Fig. 3.2 for an adsorption temperature of 125 K. For CO₂ exposures up to 0.2 L, the CO₂ coverage increases linearly. For higher CO₂ exposures, the coverage rolls over and
Figure 3.2 $^{13}$CO$_2$ (m/z = 45) TPD peak area (left ordinate) and $^{13}$CO$_2$ coverage (right ordinate) as a function of $^{13}$CO$_2$ exposure.
approaches a saturation limit. Assuming an initial sticking coefficient of unity at 125 K [105], an estimate of the upper limit of coverage (1 ML ≡ one CO$_2$ molecule per surface O$^{2-}$ anion) can be made using the kinetic theory of gases [129], along with a surface oxygen anion density of 1.0×10$^{15}$ cm$^{-2}$ based on the MnO(100) lattice parameters [39]. Applying a linear correlation to the $^{13}$CO$_2$ TPD peak area at low coverages gives the coverage scale in monolayers on the right hand side of Fig. 3.2, and a CO$_2$ saturation coverage of approximately 0.25 suggests that one CO$_2$ molecule adsorbs for every four surface O$^{2-}$ anions on MnO(100). A similar saturation coverage has been reported for CO$_2$ adsorption at 100 K on MgO(100) [105].

Preliminary DFT calculations in our group that include van der Waals corrections [130] give a heat of adsorption of CO$_2$ of 8.16 kcal·mol$^{-1}$ for a CO$_2$ molecule on a flat terrace. This value matches well with the experimental activation energy of desorption of 9.1 kcal·mol$^{-1}$ observed for the 150 K desorption feature attributed above to desorption of molecular CO$_2$ from terrace sites. Utilizing a surface step to represent a surface defect, DFT gives a heat of adsorption of 27.95 kcal·mol$^{-1}$ for molecular CO$_2$ adsorption at a step edge. While this value is significantly greater than the activation energy of desorption of 17.4 kcal·mol$^{-1}$ attributed to CO$_2$ desorption from surface defect sites, it does indicate the likelihood that higher temperature desorption features can reasonably be attributed to defect sites. Other types of defect sites (ex., cation and anion vacancies) will be explored computationally in future work.

3.2.2. Water TPD

Water TPD was used to characterize energetically-different bound forms of water on MnO(100). Fig. 3.3 shows the TPD traces of D$_2$O (m/z = 20) on MnO(100) with
Figure 3.3 TPD traces of D$_2$O (m/z = 20) following D$_2$O adsorption with dose size from 0.05 - 2.0 L on the clean and nearly-stoichiometric MnO(100) surface.
increasing D₂O coverage. For each TPD trace, the surface was cooled to 125 K, then exposed to D₂O for TPD. At the lowest dose investigated, 0.05 L, a broad D₂O desorption feature is observed in the temperature range from 240 to 600 K. For higher D₂O exposures, the portion of the desorption trace from 300 K to 600 K slowly increases in intensity, then saturates for a D₂O exposure of 0.5 L. A lower temperature portion of the desorption trace between 240 K and 300 K grows rapidly with increasing dose, and becomes the dominant feature for a D₂O exposure of 0.2 L, giving a peak maximum at 260 K. This feature saturates for a D₂O exposure of 1.0 L, with a shift in the peak temperature to 220 K. At 0.6 L of D₂O exposure, a third desorption feature appears at 170 K, and quickly rises to become the primary desorption feature with increasing coverage.

The desorption feature from 300 K to 600 K is assigned to the recombination of dissociated water since it is generally observed that water desorption from metal oxide surfaces above room temperature in UHV is due to recombinative desorption [111, 112]. Also, it has been reported that water dissociates on surface defects of MnO(100) at room temperature for water pressures up to 10⁻⁴ Torr [126], but does not adsorb on terraces at room temperature. Since the applied water pressures in our experiments do not exceed 4×10⁻⁸ Torr, it is reasonable to conclude that all the water desorption observed above 300 K is associated with the recombination of dissociated water at surface defect sites.

The second desorption feature from 200 K to 300 K with a peak maximum at 220 - 260 K is assigned to the molecular desorption of water from terraces on MnO(100). Water desorption features in a similar temperature range are reported on other rocksalt-structured metal oxide surfaces such as MgO(100) [114] and NiO(100) [122, 124], and
have been attributed to molecularly adsorbed water on terrace sites supported by spectroscopic evidences from RAIRS [114] and UPS [122] measurements. The apparent first-order activation energy for desorption of this feature ranges from 14.2 - 16.1 kcal·mol⁻¹ as estimated by Redhead analysis [128] assuming a normal pre-exponential factor of 10¹³ s⁻¹. The water desorption feature at 170 K does not saturate at the highest dose investigated, indicating desorption of a multilayer [111].

3.2.3. TPD of sequential water and CO₂ doses

TPD of sequential D₂O and ^13^CO₂ doses was used to investigate the interactions between water and CO₂ on MnO(100). Fig. 3.4 shows the TPD traces of D₂O (m/z = 20) and ^13^CO₂ (m/z = 45) following sequential 0.5 L D₂O and 0.5 L ^13^CO₂ doses on MnO(100) in both orders. For each TPD trace, the surface was cooled to 125 K before gas exposure, then TPD was run for the temperature range from 125 K to 1000 K. For comparison, the previously described TPD traces for 0.5 L of D₂O on the clean surface and 0.5 L of ^13^CO₂ on the clean surface are also included.

When D₂O is dosed prior to ^13^CO₂, the D₂O desorption features show no significant difference compared to that for D₂O alone on the clean surface, indicating that post-dosed CO₂ has little impact on pre-adsorbed water. The ^13^CO₂ desorption feature from terraces at 150 K is significantly attenuated by pre-dosed water, and the feature for ^13^CO₂ desorption from surface defects from 200 - 500 K is absent, suggesting that pre-adsorbed water blocks the uptake of CO₂ on both terrace and defect sites of MnO(100).

Reversing the order, when ^13^CO₂ is dosed prior to D₂O, the D₂O TPD peak area decreases by about 20%, indicating that pre-adsorbed CO₂ blocks a small fraction of post-dosed water. The 150 K ^13^CO₂ desorption feature from terraces is greatly attenuated,
Figure 3.4 TPD traces of D₂O (m/z = 20) and ¹³CO₂ (m/z = 45) on MnO(100) from (a) 0.5 L D₂O dose; (b) 0.5 L ¹³CO₂ dose; (c) 0.5 L ¹³CO₂ dose following 0.5 L D₂O pre-dose; (d) 0.5 L D₂O dose following 0.5 L ¹³CO₂ pre-dose.
suggesting that water displaces the majority of pre-adsorbed CO$_2$ from terrace sites. However, the most striking observation is a $^{13}$CO$_2$ desorption feature in the temperature range from 200 to 600 K with a peak maximum at 400 K. This result suggests that a fraction of pre-adsorbed CO$_2$ is stabilized by post-dosed water on MnO(100). It is not clear from the data in Fig. 3.4 whether this water-induced CO$_2$ stabilization occurs at terrace or defect sites. An apparent first-order activation energy of desorption of 25.1 kcal·mol$^{-1}$ is estimated for a pre-exponential factor of $10^{13}$ s$^{-1}$, which is higher than any $^{13}$CO$_2$ desorption feature on clean surface.

An attempt was made to determine the characteristics of the adsorption sites that are responsible for the water-induced CO$_2$ stabilization. Varying the amount of pre-dosed water followed by a fixed amount of post-dosed CO$_2$ may vary the amount of stabilized CO$_2$ which can be used to characterize the proportion of active sites on the surface for CO$_2$ stabilization. Fig. 3.5 shows the TPD traces for a fixed 0.5 L $^{13}$CO$_2$ dose interacting with 0.1 - 1.0 L of pre-dosed D$_2$O on MnO(100). D$_2$O desorption features grow with increasing water dose similar to that for D$_2$O on clean surface, while $^{13}$CO$_2$ desorption features are gradually attenuated over the entire temperature range by increasing water doses. These results are consistent with our conclusion that pre-adsorbed water blocks CO$_2$ adsorption on MnO(100). However, it is observed that at the lowest D$_2$O dose investigated (0.1 L), the $^{13}$CO$_2$ desorption feature at 400 K characteristic of the water-induced CO$_2$ stabilization is present, then is attenuated by increasing pre-adsorbed D$_2$O, and disappears for a 0.5 L of D$_2$O pre-dose. This result suggests that at very low water coverages, there are still sites available for post-dosed CO$_2$ to adsorb, interact and be stabilized by water. At larger water doses (0.5 L and above), water
Figure 3.5 TPD traces of D$_2$O (m/z = 20) and $^{13}$CO$_2$ (m/z = 45) on MnO(100) from 0.5 L $^{13}$CO$_2$ dose following (a) 0.1 L (b) 0.3 L (c) 0.5 L (d) 1.0 L D$_2$O pre-dose.
occupies and subsequently blocks all available sites for CO$_2$ stabilization. The critical dose size of 0.5 L coincides with the water dose that saturates surface defects sites, suggesting that defect sites play an important role in the water-induced CO$_2$ stabilization. Reversing the order of the dose, for a fixed amount of pre-dosed CO$_2$, varying the amount of post-dosed water may also vary the amount of stabilized CO$_2$ which can be used to characterize the proportion of active sites on the surface for CO$_2$ stabilization. Fig. 3.6 shows the TPD traces for a fixed 0.5 L $^{13}$CO$_2$ dose interacting with 0.1 - 1.0 L post-dosed D$_2$O on MnO(100). A larger D$_2$O dose results in a reduced intensity of the CO$_2$ desorption from terraces at low temperature, consistent with our conclusion that water displaces CO$_2$ on terrace sites.

However, the intensity of the 400 K $^{13}$CO$_2$ desorption feature characteristic of the water-induced CO$_2$ stabilization shows no significant change for various D$_2$O dose from 0.1 to 1.0 L, suggesting the active sites for CO$_2$ stabilization are limited, and associated with surface defects on MnO(100).

3.2.4. Mechanism of water-induced CO$_2$ stabilization

Henderson investigated CO$_2$ and water co-adsorption on single crystal TiO$_2$(110) [127]. It was found that pre-adsorbed water blocks the uptake of post-dosed CO$_2$, and post-dosed water displaces pre-adsorbed CO$_2$. These results are similar to our observations on terraces of MnO(100). Importantly, he reports that simultaneously dosed CO$_2$ and water form a H$_2$O-CO$_2$ precursor (a bound van der Waals complex) which is then catalyzed by oxygen vacancy surface defects to form bicarbonate. On TiO$_2$(110) the decomposition of the bicarbonate species gives rise to a CO$_2$ TPD peak at 213 K, higher than the temperature for CO$_2$ alone from surface defects (163 K). These results are
Figure 3.6 TPD traces of D$_2$O (m/z = 20) and $^{13}$CO$_2$ (m/z = 45) on MnO(100) from (a) 0.1 L (b) 0.3 L (c) 0.5 L (d) 1.0 L D$_2$O dose following 0.5 L $^{13}$CO$_2$ pre-dose.
similar to the observation of the water-induced CO\textsubscript{2} stabilization at surface defects on MnO(100) in this chapter, although we do not find a requirement that CO\textsubscript{2} and water be dosed simultaneously. Given that water dissociates on surface defects of MnO(100), it is likely that CO\textsubscript{2} interacts strongly with a hydroxyl group to form a bicarbonate surface species similar to that reported by Henderson. The water-induced CO\textsubscript{2} stabilization on MnO(100) gives rise to a CO\textsubscript{2} TPD peak at 400 K, indicating a significantly greater stabilization of CO\textsubscript{2} than observed on TiO\textsubscript{2}(110) [127]. Therefore, we suggest that water stabilizes CO\textsubscript{2} at surface defects on MnO(100) by the formation of bicarbonate.

3.3 Conclusion

CO\textsubscript{2} adsorbs molecularly on both terrace and defect sites, while water adsorbs molecularly on terraces and dissociatively on surfaces defects. The interaction between CO\textsubscript{2} and water on MnO(100) depends on the sequence of adsorption. Pre-adsorbed water blocks uptake of CO\textsubscript{2} on both terrace and defect sites. Post-dosed water displaces CO\textsubscript{2} on terrace sites, but stabilizes CO\textsubscript{2} on defect sites through bicarbonate formation.
Chapter 4

Oxidation of Clean and Na-precovered MnO(100)

4.1 Introduction

In the reported thermochemical water splitting cycle, the redox reactions of Mn$^{2+}$/Mn$^{3+}$ oxides play important roles. In the hydrogen evolution steps, water reacts with Na$_2$CO$_3$/MnO to produce hydrogen and release CO$_2$, while Na$^+$ intercalates into MnO to form α-NaMnO$_2$ where Mn$^{2+}$ is oxidized to Mn$^{3+}$. In the catalyst recovery steps, aqueous CO$_2$ extracts Na$^+$ from α-NaMnO$_2$ to form Na$_2$CO$_3$ and birnessite-type manganese oxides (H$_x$MnO$_2$·yH$_2$O), then the remaining manganese compound is thermally reduced from Mn$^{3+}$ to Mn$^{2+}$. Therefore, a study of the formation and redox cycles of MnO and NaMnO$_2$ may provide insight into the fundamental steps in this innovative water splitting cycle.

A number of studies have been reported for the formation of manganese oxides with various Mn oxidation states from 2+ (MnO) to 4+ (MnO$_2$) from the oxidation of manganese powder or metal films [51, 54, 55, 131]. X-ray photoelectron spectroscopy (XPS) was used to characterize various Mn oxidation states by using the Mn 2p$^{3/2}$ binding energy and the Mn 3s splitting. Despite a wide range of overlapping values reported for the Mn 2p$^{3/2}$ binding energy and Mn 3s splitting for various manganese oxides, a higher Mn 2p$^{3/2}$ binding energy and a weaker Mn 3s splitting are commonly observed for higher Mn oxidation states.
A few studies have been reported for the oxidation of well-ordered MnO(100) surfaces to higher-valence manganese oxide surfaces [42, 132]. Bayer et al. [132] produced an ordered Mn₃O₄(001) surface by oxidizing a Pd(100)-supported MnO(001) thin film. Langell et al. [42] performed the Mn²⁺/Mn³⁺ redox cycle by the oxidation of a MnO(100) single crystal surface to Mn₂O₃, with subsequent thermal reduction to Mn₃O₄ and MnO(100).

NaMnO₂ has been studied primary in electrochemistry as a novel cathode material for lithium-ion batteries because of its competitive ability for the intercalation and deintercalation of Na [133, 134]. Several synthesis methods of NaMnO₂ have been reported, such as a solid-state reaction of sodium oxide or carbonate with manganese oxides [134, 135], and hydrothermal synthesis using sodium hydroxide solutions with manganese oxides [136]. However, no data is available for the formation and characterization of NaMnO₂ on a well-defined manganese oxide surface.

In this chapter, the oxidation of clean and Na-precovered MnO(100) was investigated. X-ray photoelectron spectroscopy (XPS) was used to characterize changes in surface composition and chemical states of the surface atoms. Water was used as a probe molecule in temperature programmed desorption (TPD) to further distinguish the surfaces formed. TPD of CO₂ and water on the NaMnO₂-like surface was examined for insight into the mechanism of Na⁺ extraction from NaMnO₂ by aqueous CO₂.
4.2 Results and Discussion

4.2.1. Oxidation and characterization of clean MnO(100)

A clean and nearly-stoichiometric MnO(100) surface was prepared by ion bombardment at room temperature (Ar\(^+\) bombardment, 2 KeV) and annealing to 1000 K in UHV as described in Section 1.5. After the preparation procedure, the sample exhibits a sharp (1×1) LEED pattern characteristic of a simple termination of the rocksalt-structured (cubic) MnO bulk. As shown in Fig. 4.1(a), this surface gives a Mn 2p\(_{3/2}\) binding energy of 641.1 eV, with a shake-up satellite feature at 6.2 eV higher binding energy. Both values are in good agreement with previous reports for a clean and stoichiometric MnO(100) surface [42]. A Mn 3s splitting of 6.1 eV is observed, which also agrees with values reported for MnO [51-57]. All Mn 3s signals in this chapter were smoothed by a FFT filter to improve the signal-to-noise ratio.

The O 1s to Mn 2p XPS intensity ratio is used to estimate the surface composition. XPS gives this surface an uncorrected O 1s to Mn 2p intensity ratio of 0.24, which matches the value for a clean and stoichiometric MnO(100) surface reported by Langell et al. [42] using a different preparation method. The experimental O 1s/Mn 2p ratio for MnO(100) after correction with empirical XPS atomic sensitivity factors is 1.20, 20% greater than the ideal 1:1 stoichiometry for the MnO bulk. However, given the different kinetic energies of the Mn and O photoelectron and hence the inelastic mean free path, deviations from the bulk composition are not unexpected for a single crystal compound surface [45].

A conventional layer-by-layer summations was used to simulate the expected O/Mn ratio for the MnO(100) surface [45]. This method assumes an exponential decay.
Figure 4.1 Mn 2p$_{3/2}$, Mn 3s and O 1s XPS spectra of (a) the clean and nearly-stoichiometric MnO(100); (b) the Mn$_3$O$_4$-like surface; (c) the Mn$_2$O$_3$-like surface. Symbol S represents the shake-up satellite feature of Mn 2p$_{3/2}$.
of signal intensity with distance for normal emission, and no diffraction effect. The inelastic mean free paths of Mn and O in MnO compound were similarly predicted using the NIST Electron Inelastic-Mean-Free-Path Database [50] as described in Section I.5. This simulation gives an O/Mn ratio of 1.15, which is close to the experimental value of 1.20.

Various oxidation treatments on the clean MnO(100) surface result in the formation of Mn₃O₄-like and Mn₂O₃-like surfaces which are characterized by XPS. Di Castro and Polzonetti [51] oxidized MnO layers to Mn₂O₃ by annealing in 1 atm of O₂ at 673 K for 15 min without the intermediate formation of Mn₃O₄. Langell et al. [42] reported the formation of a Mn₂O₃ surface by annealing a MnO(100) single crystal surface in 5×10⁻⁷ Torr of O₂ at 625 K for 2.5 h. We have repeated their preparation procedures (5×10⁻⁷ - 1×10⁻⁶ Torr O₂, 625 - 673 K, up to 2.5 h) but fail to obtain a Mn₂O₃-like surface. Instead, we find Mn₃O₄-like surfaces as characterized by XPS. We find that annealing the MnO(100) surface in 1×10⁻⁶ Torr of O₂ at 673 K for 15 min is sufficient to form the Mn₃O₄-like surface as characterized by XPS and shown in Fig. 4.1(b). The Mn 2p₃/2 binding energy of 641.8 eV is 0.7 eV higher than MnO(100), indicating the presence of higher Mn oxidation states than for MnO alone (2+) [51, 55, 131]. This result is consistent with the expected mixed Mn oxidation states of 2+ and 3+ for Mn₃O₄. The measured Mn 2p₃/2 peak width (FWHM = 4.0 eV) is broadened by 0.3 eV compared to MnO(100) (3.7 eV), which may be attributed to the co-existence of two Mn oxidation states. The previously observed shake-up satellite feature for MnO disappears, consistent with literature reports for Mn₃O₄ that the satellite shifts to higher binding energies and overlaps with the Mn 2p₁/2 feature [42, 51, 53]. The Mn 3s splitting decreases to 5.6 eV,
also in agreement with values reported for Mn$_3$O$_4$ [51, 55], indicating the presence of Mn$^{3+}$. No obvious differences in the characteristics of the O 1s binding energy (530.1 eV) or peak width (2.0 eV) are observed compared to MnO(100). The O 1s/Mn 2p XPS intensity ratio for this surface is 1.55, which is 29% greater than the value observed for nearly-stoichiometric MnO(100). This increase is close to the ideal 33% increase of O/Mn stoichiometry expected for a change from MnO to Mn$_3$O$_4$. Only a diffuse background is observed in LEED, which suggests that the structure of this oxidized surface has no long-range periodicity.

In order to further oxidize Mn$_3$O$_4$ to Mn$_2$O$_3$, a mild ion bombardment followed by a UHV annealing was used to generate surface defects as an attempt to facilitate further oxidation before additional annealing in O$_2$. It is found that a Mn$_2$O$_3$-like surface, as characterized by XPS, could be formed by repeatedly treating a Mn$_3$O$_4$-like surface by ion bombardment at room temperature (Ar$^+$ bombardment, 500 eV), UHV annealing to 1000 K for 10 min, then annealing in 1×10$^{-6}$ Torr of O$_2$ at 673 K for 15 min and 625 K for 2 h. Here we need to note that this method did not always give a reproducible surface composition. Fig. 4.1(c) shows the XPS spectra of a Mn$_2$O$_3$-like surface formed by this procedure. Similar to the Mn$_3$O$_4$-like surface, the Mn 2p$_{3/2}$ binding energy of 641.8 eV and the absence of the shake-up satellite feature both indicate the presence of Mn$^{3+}$. However, with the exception of surface composition, the characteristics of the XPS signals are indistinguishable between the Mn$_2$O$_3$-like and Mn$_3$O$_4$-like surfaces. The O 1s/Mn 2p XPS intensity ratio for the Mn$_2$O$_3$-like surface in Fig. 4.1(c) is 1.85 and is 54% greater than that observed for MnO(100). This increase is close to the ideal 50% increase of O/Mn stoichiometry expected for a change from MnO to Mn$_2$O$_3$. Similar to the
Mn$_3$O$_4$-like surface, only a diffuse background is observed in LEED, suggesting the structure of this oxidized surface has no long-range periodicity.

4.2.2. Oxidation and characterization of Na-precovered MnO(100)

A NaMnO$_2$-like surface can be formed by oxidizing a metallic Na precovered MnO(100) surface. Fig. 4.2(a) shows the XPS spectra of a MnO(100) surface pre-covered with 11.5 ML of Na. Interactions between Na and MnO(100) in a non-oxidizing environment is described in Chapter 2. The appearance of plasmon loss features in both Na 1s and Na KLL spectra indicates the dominant presence of metallic Na on MnO(100) at this coverage. While the Mn and O XPS signals are greatly attenuated by the Na overlayer, the binding energies of Mn2p$_{3/2}$ and O1s, the peak width of Mn2p$_{3/2}$ and the Mn 3s splitting are similar to those for clean MnO(100).

A NaMnO$_2$-like surface was produced by annealing the 11.5 ML Na-precovered MnO(100) surface in 1×10$^{-6}$ Torr of O$_2$ at 673 K for 15 min, then briefly heating (flash) to 1000 K in UHV. This surface is characterized by XPS as shown in Fig. 4.2(b). The plasmon loss features are absent in both Na 1s and Na KLL spectra, indicating that metallic Na is no longer present. Na KLL shows a single peak feature, indicating Na in the form of a non-metallic Na compound [69, 97-99]. A Na 1s peak at 1071.2 eV is observed, which is 0.2 eV lower than that for metallic Na. In Chapter 2, we found that oxidic Na on the MnO substrate exhibits higher Na 1s binding energy than that for metallic Na, as would be normally expected. Nonetheless, although unexpected, the Na 1s binding energy of several bimetallic sodium oxides, such as NaCrO$_4$, NaAsO$_2$ and Na$_2$SeO$_3$, are reported to be 0.1 - 0.9 eV lower than that for metallic Na [99]. Due to the
Figure 4.2 Na 1s and KLL, Mn 2p\textsubscript{3/2} and 3s and O 1s XPS spectra of (a) 11.5 ML Na-precovered MnO(100); (b) the NaMnO\textsubscript{2}-like surface; (c) the NaMnO\textsubscript{2}-like surface after prolonged UHV annealing (> 10 min) at 1000 K. Symbol p represents the plasmon loss features of metallic Na and symbol S represents the shake-up satellite feature of Mn 2p\textsubscript{3/2}. 
lack of reported data for NaMnO$_2$, here we consider the measured Na 1s binding energy of NaMnO$_2$ to be consistent with those reported for other bimetallic sodium oxides. The Mn 2p$_{3/2}$ binding energy is 641.9 eV with the absence of shake-up satellite feature, and the Mn 3s splitting of this surface is 5.5 eV, which are all similar to those for the Mn$_3$O$_4$-like and Mn$_2$O$_3$-like surface and indicate the presence of Mn$^{3+}$. This result is in agreement with the expected Mn oxidation state (3+) in NaMnO$_2$ [137]. The peak width (FWHM) of Mn 2p$_{3/2}$ is 3.4 eV which is narrower than both clean (3.7 eV) and oxidized (4.0 eV) MnO(100). The O 1s signal for this surface has similar binding energy (530.1 eV) but narrower peak width (1.6 eV) compared to those for the clean and oxidized MnO(100). The surface composition estimated by XPS gives a Na:Mn:O XPS intensity ratio of 1.19:0.93:2 using atomic sensitivity factors estimated for NaMnO$_2$. This surface composition is close to that expected for NaMnO$_2$. Similar to the Mn$_3$O$_4$-like and Mn$_2$O$_3$-like surfaces, only diffuse background is observed in LEED, suggesting the structure of this surface has no long-range periodicity.

Prolonged annealing (> 10 min) of the NaMnO$_2$-like surface in UHV at 1000 K results in the reduction of Mn as shown in Fig. 4.2(c). The Mn 2p$_{3/2}$ binding energy (641.1 eV) and peak width (3.7 eV), the presence of shake-up satellite feature, and the Mn 3s splitting (6.0 eV) are all similar to those for the clean MnO(100) and characteristic of Mn$^{2+}$. These results indicate that Mn$^{3+}$ in NaMnO$_2$ is reduced to Mn$^{2+}$ by the thermal treatment in UHV of the NaMnO$_2$-like surface. Na 1s and Na KLL signals are significantly attenuated with no Na desorption signal (m/z = 23) detected in TPD. Similar observations were reported in Chapter 2 at elevated temperatures in UHV, and is attributed to the thermally-induced inward diffusion of adsorbed Na.
4.2.3. Water TPD

Water was used as a probe molecule to examine the clean and oxidized MnO(100) surfaces and the NaMnO$_2$-like surface. Fig. 4.3 shows the TPD traces of D$_2$O (m/z = 20) following 0.5 L (1 L $\equiv$ 1×10$^{-6}$ Torr·s) D$_2$O dose on the four surfaces. For each dose, the surface was cooled to 125 K prior to dosing, and TPD was run for the temperature range from 125 K to 600 K. On the clean MnO(100) exposing cations in a 2+ oxidation state, the main D$_2$O desorption feature is observed below 300 K with a peak maximum at 230 K as shown in Fig. 4.3(a). Water desorption features in a similar temperature range are reported on other rocksalt-structured metal oxide surfaces such as MgO(100) [113, 114] and NiO(100) [123, 124], and have been attributed to molecularly adsorbed water on terrace sites. The high temperature tail of the water desorption peak above 300 K is assigned to the recombination of dissociated water in agreement with most literature reports [111, 112].

Fig. 4.3(b) shows the water TPD traces on the Mn$_3$O$_4$-like surface. Similar to MnO(100), water desorbs primarily below 300 K. However two desorption features are observed at 195 K and 235 K, suggesting that two types of water adsorption sites are present. The desorption peak at 235 K is at a similar temperature to the main water desorption peak on the MnO(100) surface (Mn$^{2+}$), suggesting that it may be associated with surface Mn$^{2+}$ in Mn$_3$O$_4$. The other water desorption feature appears at lower temperature (195 K), suggesting that water binds more weakly on this type of adsorption sites.
Figure 4.3 TPD traces of D₂O (m/z = 20) following 0.5 L D₂O adsorption on (a) the clean and nearly-stoichiometric MnO(100); (b) the Mn₃O₄-like surface; (c) the Mn₂O₃-like surface; (d) the NaMnO₂-like surface.
On the Mn$_2$O$_3$-like surface exposing cations in a 3+ oxidation state, a single desorption feature is observed in Fig. 4.3(c) with a peak maximum at 190 K. This feature has a similar peak temperature compared to the lower temperature desorption feature from the Mn$_3$O$_4$-like surface. Considering that the two surfaces both likely expose surface Mn$^{3+}$ cations, the water desorption near 190 K is attributed to surface Mn$^{3+}$ cations. This conclusion is also consistent with the mixed Mn oxidation states (2+ and 3+) in Mn$_3$O$_4$. As shown in Fig. 4.3(d), on the NaMnO$_2$-like surface a single desorption peak at 182 K is observed, similar to that seen for the Mn$_2$O$_3$-like surface, and consistent with the expected Mn$^{3+}$ oxidation state in NaMnO$_2$. Therefore, water TPD appears to be sensitive to surface Mn cations in different oxidation states.

4.2.4. CO$_2$ and water TPD on the NaMnO$_2$-like surface

A TPD study of the interactions between CO$_2$, water and the NaMnO$_2$-like surface was performed in the hopes of gaining insight into the mechanism of Na$^+$ extraction from aqueous CO$_2$. TPD traces for 0.5 L CO$_2$, 0.5 L D$_2$O and sequential 0.5 L CO$_2$ and 0.5 L D$_2$O doses in both orders on the NaMnO$_2$-like surface are shown in Fig. 4.4. For each run, the surface was cooled to 125 K before gas exposure, then TPD was run for the temperature range from 125 K to 600 K. For CO$_2$ alone in Fig. 4.4(a), the primary CO$_2$ desorption features are below 300 K, indicating that Na in the NaMnO$_2$-like surface does not strongly bind CO$_2$, in contrast to observations for oxidic Na adatoms on MnO(100) seen in Chapter 2. For D$_2$O alone in Fig. 4.4(b), the single D$_2$O desorption feature at 182 K is associated with surface Mn$^{3+}$ as discussed in Section 4.2.3. For sequential D$_2$O and CO$_2$ doses, when D$_2$O is dosed prior to CO$_2$ as shown in Fig. 4.4(c),
Figure 4.4 TPD traces of CO\textsubscript{2} (m/z = 44) and D\textsubscript{2}O (m/z = 20) from the NaMnO\textsubscript{2}-like surface following (a) a 0.5 L CO\textsubscript{2} dose; (b) a 0.5 L D\textsubscript{2}O dose; (c) a 0.5 L CO\textsubscript{2} dose following a 0.5 L D\textsubscript{2}O pre-dose; (d) a 0.5 L D\textsubscript{2}O dose following a 0.5 L CO\textsubscript{2} pre-dose.
the CO₂ desorption features are significantly attenuated compared to that for CO₂ alone on the NaMnO₂-like surface, while the D₂O desorption features show no significant difference compared to that for D₂O alone on the NaMnO₂-like surface. These results suggest that water blocks the uptake of CO₂ on the NaMnO₂-like surface. Similar TPD results are observed when CO₂ is dosed prior to D₂O, indicating that water displaces pre-adsorbed CO₂ from the NaMnO₂-like surface.

In the recovery steps of the reported thermochemical water splitting cycle, CO₂ is bubbled through an aqueous suspension of NaMnO₂ at 80°C to extract Na⁺ from NaMnO₂ to form Na₂CO₃ and protonic birnessite-type manganese oxides (HₓMnO₂·yH₂O). In Chapter 5, the decomposition of Na₂CO₃ on MnO(100) gives rise to a high temperature CO₂ TPD desorption peak around 800 K. However in this study, the majority of adsorbed CO₂ on the NaMnO₂-like surface desorbs below 300 K with no high temperature (> 300 K) CO₂ desorption peak observed, suggesting no strong interaction between CO₂ and Na in NaMnO₂ under the conditions of our study, and no sign of the formation of Na₂CO₃. In Chapter 3, water is found to stabilize pre-adsorbed CO₂ (likely near surface defects) on MnO(100), leading to an increase in temperature of the CO₂ desorption to 400 K, presumably resulting from the decomposition of bicarbonate species. However a similar stabilization is not observed on the NaMnO₂-like surface, suggesting no strong interactions between CO₂ and Na in the presence of water on the NaMnO₂-like surface and no formation of sodium bicarbonate. These results for NaMnO₂ indicate that our simple TPD study with D₂O and CO₂ adsorption at low temperature in UHV provides no real insight into the mechanism of Na⁺ extraction by aqueous CO₂. Given that carbon dioxide and water desorb primarily below 300 K in our study, it is likely that the
activation barrier for the Na$^+$ extraction reaction exceeds those for the simple desorption of CO$_2$ and D$_2$O in our TPD experiments.

4.3 Conclusion

The Mn$_3$O$_4$-like and Mn$_2$O$_3$-like surfaces can be formed in UHV by the oxidation of the clean and nearly-stoichiometric MnO(100). The NaMnO$_2$-like surface is produced by oxidation of the MnO(100) pre-covered by a high coverage of metallic Na. No long range order is observed for these oxidized surfaces. Water is sensitive to Mn oxidation state, and desorbs at different temperatures from the manganese oxide surfaces dependent on the Mn oxidation state. On the NaMnO$_2$-like surface, pre-adsorbed water blocks the uptake of CO$_2$, and water displaces pre-adsorbed CO$_2$. No strong interaction between CO$_2$, water and the NaMnO$_2$-like surface is observed under the conditions of our study.
Chapter 5

O₂ Adsorption on Na-precovered MnO(100)
and CO₂ Adsorption

5.1 Introduction

In the hydrogen evolution steps of the reported thermochemical water splitting cycle [22], Na₂CO₃ reacts with MnO in the presence of water to form NaMnO₂ and release CO₂ and hydrogen. The proposed pathway for this reaction is that Na₂CO₃ decomposes to CO₂, while Na⁺ intercalates into MnO to form α-NaMnO₂ where Mn²⁺ is oxidized to Mn³⁺ by oxygen provided from water. Therefore, the formation of carbonates as well as their interactions with MnO may provide insight into the reaction mechanisms of this innovative water splitting cycle.

The oxidation of alkali metals has been investigated primarily for applications in heterogeneous catalysis [58-62], the oxidation of semiconductor surfaces [138-141] and cathode materials for electrochemical energy storage [142, 143]. The oxidation of alkali metals on metal substrates can give regular alkali metal oxide (M₂O), peroxide (M₂O₂) and superoxide (MO₂) which have been characterized by XPS O 1s binding energies in the range of 527 - 531 eV, 531 - 533 eV and above 534 eV, respectively [144-146]. For the oxidation of Na on model surfaces, Na₂O and Na₂O₂ were formed by oxygen adsorption on Na-precovered Si(113) [147], while Na₂O overlayers were prepared by oxidation of Na-precovered Pd(100) [148].
Na$_2$CO$_3$ formation on model metal or metal oxide surfaces has been accomplished via two different reaction mechanisms. One method utilizes the interaction of CO$_2$ and Na$_2$O. Onishi et al. [148] oxidized Na-precovered Pd(100) to form Na$_2$O overlayers, with the adsorption of CO$_2$ on Na$_2$O thin films resulting in the formation of Na$_2$CO$_3$ on Pd(100). On TiO$_2$(110), deposited Na binds strongly to surface lattice oxygen of TiO$_2$ to form “Na$_2$O-dimer” units which sorb CO$_2$ to form carbonates [149]. A second approach is to directly expose metallic Na to CO$_2$. Seiferth et al. [101] studied CO$_2$ adsorption on Na-precovered Cr$_2$O$_3$(0001) at 90 K and found that CO$_2$ chemisorbs on Na, presumably in a NaCO$_2$ stoichiometry. Elevating the substrate temperature leads to a disproportionation reaction of chemisorbed CO$_2$ on Na to form Na$_2$CO$_3$ and release CO: 

$$2\text{NaCO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}.$$  

Similar disproportionation reactions and Na$_2$CO$_3$ formation were reported for CO$_2$ adsorption on Na-precovered Pd(111) [150], TiO$_2$(110) [151] and Fe$_3$O$_4$(111) [152].

We have previously studied the interaction between Na and MnO(100) in a non-oxidizing environment in Chapter 2. It was found that Na interacts strongly with the MnO substrate in an oxidic form up to 1 ML Na coverage. This form of Na is irreversibly-adsorbed and diffuses into the MnO bulk at elevated temperatures above 500 K. For Na coverages above 1 ML, metallic Na islands nucleate and grow on top of the Na monolayer and desorb from the surface at 430 K in TPD. In addition, the oxidation of a MnO(100) surface precovered with multilayers of (metallic) Na has also been investigated in Chapter 4. Annealing a surface precovered with 11.5 ML Na on MnO(100) in 1×10$^{-6}$ Torr of O$_2$ at 673 K for 15 min followed by flashing to 1000 K in UHV produces a NaMnO$_2$-like surface.
In this chapter, the oxidation products of Na-precovered MnO(100) at 125 K and 350 K are identified. X-ray photoelectron spectroscopy (XPS) was used to characterize changes in chemical states of surface atoms. CO$_2$ was used as a probe molecule in temperature programmed desorption (TPD) to characterize the oxidized surfaces. The formation of Na$_2$O and Na$_2$CO$_3$ is described.

5.2 Results and Discussion

For each oxidation experiment, 3 ML of Na was deposited on MnO(100) which leads to both oxidic Na in the first monolayer and metallic Na islands (Chapter 2). Exposures of 200 L (1 L $= 1 \times 10^{-6}$ Torr·s) of O$_2$ were used for subsequent oxidation. Two oxidation temperatures, 125 K and 350 K, were examined as routes for the formation of Na$_2$O on MnO(100). The surface oxidized at 350 K was also flashed to consecutively higher temperatures to characterize the thermal evolution of the oxidation products by XPS. TPD after oxidation was used to further characterize the thermal evolution of the oxidation products. In addition, CO$_2$ TPD was used to further characterize surface Na species after oxidation at 350 K and subsequent thermal treatments.

5.2.1. XPS

5.2.1.1. Na oxidation at 125 K

Fig. 5.1(a) shows the XPS spectra of the MnO(100) precovered with 3 ML of Na. XPS spectra were taken at 125 K. The single O 1s peak at 530.1 eV arises from the lattice oxygen of the MnO substrate. The appearance of plasmon loss features in both Na 1s and Na KLL spectra indicates the presence of metallic Na on MnO(100) [69, 77, 97, 98]. The Mn 2p$_{3/2}$ binding energy (not shown) is similar to that for clean MnO(100) and
Figure 5.1 O 1s, Na 1s and Na KLL XPS spectra of (a) 3 ML Na precovered MnO(100); (b) the 3ML Na precovered MnO(100) exposed to 200 L of O₂ at 125 K; (c) the 3ML Na precovered MnO(100) exposed to 200 L of O₂ at 350 K; the surface oxidized at 350 K successively heating to (d) 750 K; (e) 850 K; (f) 1000 K. Symbol p represents plasmon loss features for metallic Na.
is characteristic of Mn$^{2+}$. These results are consistent with our previous study in Chapter 2.

Fig. 5.1(b) shows the XPS spectra of a 3 ML Na precovered MnO(100) surface after exposure to 200 L of O$_2$ at 125 K. The Na 1s binding energy shifts to 1072.1 eV, and a new Na KLL feature appears at 263.4 eV. No plasmon loss features are observed in Na 1s spectra indicating the absence of metallic Na, however in the Na KLL spectra the feature at 259.5 eV and plasmon loss features characteristic of metallic Na are greatly attenuated but still present. In the O 1s spectra, besides the main peak at 530.1 eV attributed to the lattice oxygen in the MnO substrate, two shoulders are observed at 532.5 eV and 528.6 eV.

In Fig. 5.1(b), the Na 1s binding energy shifts to a higher value by 0.5 eV compared to that for metallic Na, which is close to the reported 0.7 eV increase for the oxidation of metallic Na to Na$_2$O [64, 77, 98]. The 3.9 eV increase of the new Na KLL feature at 263.4 eV compared to that for metallic Na (259.5 eV) is also similar to reports for Na oxidation to Na$_2$O [98]. Therefore, we conclude that Na$_2$O is formed by the oxidation of metallic Na at 125 K. The appearance of plasmon loss features in the Na KLL spectra but not in the Na 1s spectra can be attributed to the difference in the mean free paths of the emitted electrons. Given that Na 1s features are more surface sensitive than those for Na KLL because of their lower kinetic energy (higher binding energy), the difference in the Na features indicate that the surface of the metallic Na islands is oxidized upon interacting with O$_2$ at 125 K, while the inner core retains some metallic Na due to the limited mobility of Na and O atoms at 125 K. Thus an incomplete oxidation of the metallic Na islands occurs at 125 K.
The two O 1s shoulders at 532.5 eV and 528.6 eV in Fig. 5.1(b) arise from different oxidation products. Studies of oxygen adsorption on Ag(110) at 135 K [153] and Ag(111) at 150 K [154] report an O 1s peak in a binding energy range (528.1 - 528.3 eV) similar to the 528.6 eV feature, and has been attributed to atomic oxygen [155] which recombines to molecular oxygen and desorbs below 600 K [153, 154]. In another study of oxygen adsorption on Si(111) below 150 K [156, 157], an XPS O 1s feature at 530.5 eV was observed which is 1.1 eV lower than that for the main oxide SiO₂, similar to the 1.5 eV decrease observed for the 528.6 eV feature from the main line associated with MnO. This O 1s feature has been attributed to a metastable molecular oxygen precursor as characterized by UPS, XAES and NEXAFS, which converts to oxygen anions below 450 K. We tentatively assign the O 1s feature at 528.6 eV to an atomic oxygen surface species. The other O 1s shoulder at 532.5 eV is at higher O 1s binding energy than that for oxygen in MnO, presumably arising from a different oxidation product. Since Na₂O is the likely oxidation product based on the Na XPS results, we assign the O 1s feature at 532.6 eV to Na₂O.

In summary, an incomplete oxidation of the metallic Na islands on MnO(100) occurs at 125 K, giving Na₂O and atomic oxygen. No obvious change in the Mn 2p₃/₂ binding energy (not shown) is observed compared to that for the clean MnO(100), indicating no significant change in the Mn oxidation state (2+).

5.2.1.2. Na oxidation at 350 K

Oxidation of Na-precovered MnO(100) was also performed at 350 K in an attempt to enhance the oxidation of metallic Na to Na₂O. It was found in Chapter 2 that at an elevated substrate temperature of 350 K in UHV, metallic Na does not desorb from
MnO(100) in TPD, and no thermally-induced chemical change is observed for the deposited Na as characterized by XPS, thus making this temperature suitable for the oxidation of Na-precovered MnO(100). In addition, Onishi et al. [148] were able to prepare Na$_2$O overlayers on Pd(100) by repeatedly depositing Na on the substrate followed by O$_2$ exposure at 350 K.

Fig. 5.1(c) shows the XPS spectra of the 3 ML Na-precovered MnO(100) surface after exposure to 200 L of O$_2$ at 350 K. Compared to the 125 K oxidation results in Fig. 5.1(b), binding energies of Na 1s and Na KLL both shift to higher values at 1072.5 eV and 264.5 eV, respectively. No plasmon loss features characteristic of metallic Na are apparent in either the Na 1s and Na KLL spectra. The O 1s feature at 528.6 eV seen in Fig. 5.1(b) is not observed, and the high binding energy O 1s feature at 532.5 eV attributed to Na$_2$O is replaced by a feature at 1.1 eV higher binding energy (533.6 eV).

The absence of plasmon loss features indicates that all the metallic Na has been oxidized. The binding energy values for Na 1s, Na KLL and O 1s are higher than those expected for Na$_2$O in Fig. 5.1(b), suggesting Na surface species with a higher net level of oxidation than Na$_2$O. However the 1.1 eV increase of in O 1s binding energy to 533.6 eV is less than the 2 eV increase reported for the oxidation of Na$_2$O to Na$_2$O$_2$ [144-146]. This result suggests the presence of overlapping Na$_2$O and Na$_2$O$_2$ signals. Therefore, we tentatively assign the O 1s feature at 533.6 eV to a mixture of Na$_2$O and Na$_2$O$_2$. In summary, a complete oxidation of metallic Na islands on MnO(100) occurs at 350 K, and is thought to give mixture of Na$_2$O and Na$_2$O$_2$. 

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5.2.1.3. Thermal evolution of the Na oxidation products

A thermal treatment involving the sequential heating of the oxidized surface to successively higher temperatures in UHV was used to examine the thermal evolution of the oxidation products. After oxidation at 350 K and flashing to 750 K (Fig. 5.1d), the Na 1s and Na KLL binding energies shift to lower values at 1071.8 eV and 263.3 eV, respectively. The previously observed O 1s high binding energy feature at 533.6 eV in Fig. 5.1(c) shifts down to 532.6 eV. After flashing to 850 K (Fig. 5.1e), the Na 1s and Na KLL binding energies shift further to lower values at 1071.3 eV and 262.4 eV, respectively. The O 1s high binding energy feature at 523.6 eV in Fig. 5.1(d) disappears, and a single feature at 530.1 eV is present. After flashing to 1000 K (Fig. 5.1f), the Na 1s and KLL binding energies shift to higher values at 1071.8 eV and 263.2 eV, respectively, and a single O 1s feature at 530.1 eV is observed.

After flashing to 750 K, the O 1s high binding energy feature at 532.6 eV in Fig. 5.1(d) is similar to the one at 532.5 eV in Fig. 5.1(b), which has been assigned to Na$_2$O. This result indicates the presence of Na$_2$O on the surface oxidized at 350 K after flashing to 750 K. It has been reported that in an oxygen-rich environment with 1 atm O$_2$, Na$_2$O$_2$ decomposes to Na$_2$O at around 780 K [158, 159]. The UHV environment in our study has an extremely low oxygen partial pressure that should favor the reduction. Therefore, we conclude that after flashing to 750 K, any Na$_2$O$_2$ on the oxidized surface reduces to Na$_2$O, leaving Na$_2$O as the primary sodium compound remaining on MnO(100). The Na 1s and Na KLL binding energies in Fig. 5.1(d) are similar to those assigned to Na$_2$O in Fig. 5.1(b), consistent with this conclusion. No obvious change in the Mn 2p$_{3/2}$ binding
energy (not shown) is observed compared to that for the clean MnO(100), indicating no significant change in Mn oxidation state (2+).

After flashing to 850 K (Fig. 5.1e), the Na 1s and Na KLL binding energies at 1071.3 eV and 262.4 eV, respectively, both match values observed for NaMnO₂ prepared on MnO(100) by a different approach in Chapter 4. The Mn 2p₃/₂ binding energy of 641.7 eV (not shown) characteristic of Mn³⁺ (Chapter 4) is observed, consistent with the expected Mn³⁺ oxidation state in NaMnO₂. Therefore, we conclude that NaMnO₂ is present on MnO(100) after flashing to 850 K. Given that the O 1s feature at 532.6 eV for Na₂O is absent in Fig. 5.1(e), we suggest that NaMnO₂ is formed via a solid state reaction of Na₂O and MnO. In the reported thermochemical water splitting cycle [22], a reaction of Na₂CO₃ and MnO in the presence of water gives NaMnO₂ and CO₂, while water is reduced to hydrogen. The solid state reaction of Na₂O and MnO to form NaMnO₂ observed in this work suggests a similar reaction, given that Na₂O is a likely reaction product from the decomposition of Na₂CO₃ to release CO₂.

In our previous work on the formation of NaMnO₂ by a different approach (Chapter 4), a NaMnO₂-like surface formed by the oxidation of 11.5 ML of Na on MnO(100) decomposes upon heating to 1000 K in UHV for more than 10 min. After flashing the surface in Fig. 5.1(e) to 1000 K (Fig. 5.1f), the Na 1s and KLL binding energies are similar to those obtained after the decomposition of NaMnO₂ in Chapter 4, and the Mn 2p₃/₂ binding energy (not shown) shifts to 641.1 eV which is characteristic of Mn²⁺. Therefore, we suggest the NaMnO₂ formed by a solid state reaction between Na₂O and MnO thermally decomposes above 850 K.
5.2.2. TPD after Na oxidation

TPD traces following a 200 L O\textsubscript{2} dose on the 3 ML Na-precovered MnO(100) surface at 125 K and 350 K are shown in Fig. 5.2. In the TPD traces from the surface oxidized at 125 K (Fig. 5.2a), no direct desorption of sodium oxide species such as Na\textsubscript{2}O\textsubscript{2} (m/z = 78) or Na\textsubscript{2}O (m/z = 62) is detected. A low temperature O\textsubscript{2} desorption feature is observed below 400 K, and a broad O\textsubscript{2} desorption signal is present above 620 K. A sharp Na desorption feature is observed at 420 K, and a broad Na desorption signal is present between 690 K and 820 K.

The low temperature O\textsubscript{2} feature below 400 K may be associated with a recombinative desorption of the atomic oxygen identified by XPS in Fig. 5.1(b). The broad high temperature O\textsubscript{2} desorption above 620 K is attributed to the thermal decomposition of Na\textsubscript{2}O. Na desorption at 420 K is similar to the desorption of metallic Na at 430 K (Chapter 2), indicating the presence of metallic Na on the surface, and consistent with the incomplete oxidation of metallic Na at 125 K observed in XPS. The high temperature Na desorption between 690 K and 820 K is in the same temperature range as that for the high temperature O\textsubscript{2} desorption above 620 K, consistent with the thermal decomposition of Na\textsubscript{2}O. We note that the high temperature O\textsubscript{2} and Na desorption traces represent a small fraction of the total amount of surface oxygen and Na. The desorbed amount of O\textsubscript{2} is less than that from a 0.1 L dose of O\textsubscript{2} on clean MnO(100) at 125 K, and the amount of desorbed Na is equivalent to only about 0.16 ML of metallic Na by comparison to our earlier work in Chapter 2. This result suggests that a majority of Na\textsubscript{2}O reacts with MnO to form NaMnO\textsubscript{2} above 750 K, as characterized by XPS.
Figure 5.2 TPD traces of \( \text{O}_2 \) (m/z = 32) and \( \text{Na} \) (m/z = 23) from a 200 L \( \text{O}_2 \) dose on a 3 ML Na precovered MnO(100) surface at (a) 125 K; (b) 350 K.
In the TPD traces from the surface oxidized at 350 K (Fig. 5.2b), no Na desorption is observed around 430 K indicating no metallic Na is present on the surface, consistent with the complete oxidation of metallic Na at 350 K observed in XPS. O₂ desorption above 640 K and Na desorption between 690 K and 820 K are observed, both similar to those in Fig. 5.2(a), which has been attributed to the thermal decomposition of Na₂O.

5.2.3. CO₂ TPD

CO₂ was used as a probe molecule to characterize surface sodium species after oxidation at 350 K and thermal treatment at higher temperatures in UHV. After each surface was prepared, it was cooled to 125 K before ¹³CO₂ exposure, then TPD was run for the temperature range from 125 K to 1000 K. ¹⁸O-labeled O₂ was used for the oxidation treatments in this section to generate ¹⁸O-containing sodium oxide surface species. Monitoring oxygen exchange between ¹³CO₂ and ¹⁸O-labeled surface oxide species characterized by TPD traces of ¹³C₁⁶O₂ (no exchange), ¹³C₁⁶O₁⁸O (single exchange) and ¹³C¹⁸O₂ (double exchange) can provide information about the binding of CO₂ on the surface oxide species.

Fig. 5.3(a) shows the TPD traces of ¹³CO₂ (m/z = 45) and ¹³CO (m/z = 29) from the surface precovered with 2.33 ML of Na with metallic Na present (no oxidation) as described in Chapter 2. The strong binding of CO₂ with metallic Na gives rise to a broad, high temperature ¹³CO₂ desorption feature at 735 K. Just under 20% of the CO₂ adsorbed on metallic Na goes through a disproportionation reaction [101]: 2NaCO₂ → Na₂CO₃ + CO as evidenced by the broad ¹³CO signal between 450 K and 800 K.
Figure 5.3 TPD traces following a 0.5 L $^{13}$CO$_2$ dose on (a) 2.33 ML Na precovered MnO(100); (b) 3 ML Na precovered MnO(100) exposed to 200 L of O$_2$ at 350 K; and the surface oxidized at 350 K after flashing to (c) 750 K and (d) 850 K.
Fig. 5.3(b) shows the CO$_2$ TPD traces from a 3 ML Na precovered MnO(100) surface after oxidation with 200 L of $^{18}$O$_2$ at 350 K. A high temperature CO$_2$ desorption feature at 800 K is observed with a smaller peak at 705 K. For both features, oxygen exchange is observed with similar ratios of 0.2:0.5:0.3 of $^{13}$C$^{16}$O$_2$ (no exchange), $^{13}$C$^{16}$O$^{18}$O (single exchange) and $^{13}$C$^{18}$O$_2$ (double exchange) observed. No CO desorption signal is detected. If a similarly prepared surface is first flashed to 750 K before CO$_2$ adsorption (Fig. 5.3c), the CO$_2$ desorption feature at 705 K in Fig. 5.3(b) is absent, while the feature at 800 K is present but attenuated. A ratio of 0.2:0.5:0.3 of $^{13}$C$^{16}$O$_2$ (no exchange), $^{13}$C$^{16}$O$^{18}$O (single exchange) and $^{13}$C$^{18}$O$_2$ (double exchange) is observed for the 800 K feature, similar to what was seen in Fig. 5.3(b). A low temperature CO$_2$ desorption feature near 150 K is also observed, and a small, broad CO$_2$ desorption feature is present from 200 K to 500 K. No CO desorption signal is detected. Since a mixture of Na$_2$O and Na$_2$O$_2$ are the expected products following oxidation at 350 K as identified by XPS, the high temperature CO$_2$ desorption features at 705 K and 800 K in Fig. 5.3(b) are attributed to the strong binding of CO$_2$ to Na$_2$O and Na$_2$O$_2$. After flashing to 750 K, only the 800 K CO$_2$ desorption feature is present, and the XPS results indicate that Na$_2$O is the only sodium oxide species remaining on the surface after this treatment. Therefore, the CO$_2$ desorption feature at 800 K in Fig. 5.3(c) (as well in Fig. 5.3b) is attributed to a strong chemical interaction between CO$_2$ and Na$_2$O. The absence of the CO$_2$ desorption feature at 705 K after flashing to 750 K (Fig. 5.3c) coincides with the thermal decomposition of Na$_2$O$_2$ to Na$_2$O observed in XPS after flashing to 750 K, thus the 705 K feature is tentatively assigned to the interaction between CO$_2$ and Na$_2$O$_2$. We note that the temperature range of the 705 K feature also
overlaps with the temperature for CO$_2$ chemisorbed on metallic Na shown in Fig. 5.3(a). However given that a complete oxidation of metallic Na occurs at 350 K as characterized by XPS and TPD after oxidation, a contribution from chemisorbed CO$_2$ on metallic Na is ruled out. Additionally, the absence of CO desorption indicates that no CO$_2$ disproportionation reaction occurs from adsorbed CO$_2$, again suggesting that no metallic Na is present.

The observation of oxygen exchange between CO$_2$ and surface oxides is an indication of carbonate formation [160-163]. Oxygen exchange has been reported between CO$_2$ and several metal oxides such as MgO [160-163] and Al$_2$O$_3$ [164]. Fig. 5.4 illustrates the proposed mechanism of single and double oxygen exchange for CO$_2$ on MgO(100) [161, 163]. It was found that, when the MgO(100) surface is exposed to CO$_2$ (Fig. 5.4a), bidentate carbonate must be present after CO$_2$ adsorption in order for an oxygen exchange (single and double) to occur [160-163], with C in CO$_2$ (O$^3$=C=O$^4$) bonding to surface O$^1$, and O$^3$ in CO$_2$ bonding to an adjacent surface Mg$^1$ (Fig. 5.4b) [160, 161, 163]. A single oxygen exchange is thought to occur by breaking the C-O$^3$, Mg$^1$-O$^1$ and Mg$^2$-O$^1$ bonds to give O$^1$=C=O$^4$ [160, 161, 163]. If the C-O$^3$ bond breaks to give a new bidentate carbonate in Fig. 5.4(c), and the bidentate carbonate “rolls over” without leaving the surface (Fig. 5.4c to 5.4e), a second oxygen exchange is ready for the bidentate carbonate in Fig. 5.4(e) [161, 163]. Since significant oxygen exchange is observed in CO$_2$ desorption features from Na$_2$O and Na$_2$O$_2$ in TPD (Fig. 5.3b), we conclude that Na$_2$CO$_3$ is formed by the interaction between CO$_2$ and Na$_2$O and Na$_2$O$_2$, and decomposes to give CO$_2$ desorption features at 705 K and 800 K in Fig. 5.3(b). We note that while C 1s XPS can generally be used to characterize changes in chemical states
**Figure 5.4** Illustration of the proposed mechanism for single and double oxygen exchange between CO$_2$ and MgO(100) in Ref. [161, 163]. Figure adapted from Fig. 6 in Ref. [161].
of surface carbon to distinguish between molecularly adsorbed CO$_2$ and carbonate, the C 1s signal in this work overlaps with the much more intense features of Na KLL spectra, thus no usable information about the carbonate formation is obtained from C 1s XPS measurements.

The low temperature CO$_2$ desorption feature near 150 K and the small, broad CO$_2$ desorption feature from 200 K to 500 K after flashing to 750 K (Fig. 5.3c) are similar to the CO$_2$ TPD features observed from terraces and defects of MnO(100) respectively in Chapter 3. This result suggests a partially exposed MnO(100) surface, which can be formed by the inward diffusion of the oxidic Na in the first monolayer that occurs above 500 K as seen in Chapter 2. We note that the small amount of $^{13}$C$^{16}$O$^{18}$O (6%) at 150 K is due to the uptake of background CO$_2$ at m/z = 47 which is observed in the chamber after multiple isotope-exchange experiments.

If a Na-precovered surface is oxidized and flashed to 850 K prior to CO$_2$ exposure (Fig. 5.3d), a CO$_2$ desorption feature at 150 K and broad CO$_2$ desorption features from 200 K to 700 K are observed, similar to those on either a NaMnO$_2$-like surface (Chapter 4) or MnO(100) in Fig. 5.3(c). The CO$_2$ desorption feature at 800 K in Fig. 5.3(c) is not observed. The absence of a CO$_2$ desorption feature at 800 K which has been attributed to the decomposition of Na$_2$CO$_3$ formed by the reaction of CO$_2$ and Na$_2$O, indicates the absence of surface Na$_2$O, consistent with the suggestion of a solid state reaction between Na$_2$O and MnO(100) to form NaMnO$_2$ near 850 K, as proposed from the XPS data.

5.2.4. Engineering a surface exposing both Na$_2$CO$_3$ and MnO(100)

In the reported thermochemical water splitting cycle [22], water splits to produce hydrogen over a mechanical mixture of Na$_2$CO$_3$ and MnO. Modeling such a complex
mixed oxide system is thought to be important for gaining insight into the reaction mechanisms of hydrogen evolution, but can be challenging when starting with a single crystal MnO substrate in UHV.

In this work, efforts have been made to produce a surface exposing both Na₂CO₃ and MnO(100) to model the mixed oxide surface of Na₂CO₃/MnO. Fig. 5.5(a) to (d) are cartoons illustrating the morphology and composition of the surface as a function of a specific synthetic procedure described below. CO₂ TPD characterization of the resulting surface is shown in Fig. 5.5(e).

We start with a clean MnO(100) single crystal surface and deposit 3 ML of Na on MnO(100). It has been found in our previous study of Na deposition on MnO(100) (Chapter 2) that, for a multilayer Na coverage, oxidic Na on MnO(100) is formed for the first monolayer of deposited Na, followed by the growth of metallic Na islands. The 3 ML Na precovered MnO(100) surface is illustrated by a simple cartoon in Fig. 5.5(a).

In the second step, the 3 ML Na precovered MnO(100) surface is exposed to 200 L of O₂ at 350 K to form Na₂O and Na₂O₂ on MnO(100) from metallic Na as characterized by XPS in Section 5.2.1. Therefore, a MnO(100) surface covered with oxidic Na in the first monolayer and sodium oxide (Na₂O and Na₂O₂) islands is prepared as illustrated in Fig. 5.5(b).

The third step is to expose the surface from the above treatments (Fig. 5.5b) to 0.5 L of CO₂ at 125 K to form Na₂CO₃ on MnO(100). It is found in this work that, CO₂ interacts strongly with Na₂O and Na₂O₂ to form Na₂CO₃ as characterized by CO₂ TPD in Section 5.2.3. Therefore, a MnO(100) surface covered with oxidic Na in the first monolayer and Na₂CO₃ islands is prepared, as illustrated in Fig. 5.5(c).
Figure 5.5 (a) to (d): cartoons illustrating the morphology and composition of surface as a function of synthetic procedure for a surface exposing Na$_2$CO$_3$ islands on MnO; (e) CO$_2$ TPD traces following a 0.5 L $^{13}$CO$_2$ dose on the engineered surface (d) exposing Na$_2$CO$_3$ islands on MnO.
The remaining task is to remove the oxidic Na in the first monolayer and subsequently partially expose portions of the MnO(100) surface. It has been found in Chapter 2 that the oxidic Na in the first monolayer can be driven into the MnO subsurface by heating to 600 K for 10 min in UHV. This temperature is high enough to remove chemisorbed CO$_2$ from oxidic Na in the first monolayer (Chapter 2), and considerably lower than that for the thermal decomposition of a majority of Na$_2$CO$_3$ around 800 K (as characterized by CO$_2$ TPD in Section 5.2.3), and also lower than the temperature required for the solid state reaction of Na$_2$O and MnO to form NaMnO$_2$ above 750 K (as characterized by XPS in Section 5.2.1 and CO$_2$ TPD in Section 5.2.3). Therefore, heating the MnO(100) surface covered with oxidic Na in the first monolayer and Na$_2$CO$_3$ islands in Fig. 5.5(c) to 600 K for 10 min in UHV should drive the oxidic Na in the first monolayer into the MnO subsurface without introducing notable thermal changes to Na$_2$CO$_3$ islands, and give a surface exposing Na$_2$CO$_3$ islands on MnO(100) as illustrated in Fig. 5.5(d).

CO$_2$ TPD was used to characterize the surface prepared by the outlined synthetic strategy. TPD traces of $^{13}$CO$_2$ (m/z = 45) are shown in Fig. 5.5(e) following a 0.5 L CO$_2$ dose on the engineered surface at 125 K. A low temperature CO$_2$ desorption feature near 150 K is observed, along with a small, broad feature from 200 K to 500 K, and a high temperature CO$_2$ desorption feature at 800 K with a shoulder around 720 K. The CO$_2$ desorption feature at 150 K and the broad feature from 200 K to 500 K are similar to the desorption features from CO$_2$ adsorption on terraces and defects of MnO(100), respectively, confirming the exposure of bare MnO(100). The CO$_2$ desorption feature at 800 K with a shoulder around 720 K is similar to the ones from the decomposition of
Na$_2$CO$_3$ formed by the interaction between CO$_2$ and sodium oxides as characterized by CO$_2$ TPD in Section 5.2.3, indicating the presence of Na$_2$CO$_3$. We conclude that the synthetic procedure allows us to engineer a surface exposing Na$_2$CO$_3$ islands on MnO(100) as illustrated in Fig. 5.5(d).

5.3 Conclusion

Na$_2$O and atomic oxygen are formed by the oxidation of a multilayer coverage of Na on MnO(100) at 125 K, while Na$_2$O and Na$_2$O$_2$ are formed at 350 K. Na$_2$O reacts with the MnO(100) substrate to form NaMnO$_2$ below 850 K. CO$_2$ interacts strongly with Na$_2$O and Na$_2$O$_2$ to form Na$_2$CO$_3$. A surface exposing Na$_2$CO$_3$ islands on MnO(100) has been engineered to model the complex Na$_2$CO$_3$/MnO mixed oxide used for hydrogen evolution in the reported thermochemical water splitting cycle [22].
Chapter 6

Reaction of Water with Na-pretreated MnO(100)

6.1 Introduction

In the hydrogen evolution steps of the thermochemical water splitting cycle of Xu et al. [22], water splits to hydrogen on a mixture of Na$_2$CO$_3$ and MnO, while Na$_2$CO$_3$ reacts with MnO to form NaMnO$_2$ and release CO$_2$. The authors suggest that Na$_2$CO$_3$ is the critical component for the hydrogen evolution from water. Na$^+$ in Na$_2$CO$_3$ intercalates into MnO and enables the oxidation of Mn$^{2+}$ in MnO to Mn$^{3+}$ in NaMnO$_2$ by water, while water is reduced to hydrogen. Therefore, water adsorption on the surface combining MnO and Na$_2$CO$_3$, as well as the ones combining MnO and components of Na$_2$CO$_3$ (e.g. Na$_2$O and Na), are of our interests for the study of hydrogen evolution from water. This study may suggest the nature of active component responsible for hydrogen evolution under the conditions of our study, and provide insight into the reaction mechanisms of the thermochemical water splitting.

In this chapter, water TPD is performed on several surfaces to determine if any single components or combinations of materials can give rise to hydrogen evolution from water in a traditional UHV surface science environment. Surfaces combining Na and MnO in a non-oxidizing environment have been studied in Chapter 2. Two types of Na are identified: oxidic Na in the first monolayer on MnO(100), and metallic Na islands for multilayer Na coverages. The reaction of water with both of these types of Na on MnO(100) will be examined.
In Chapter 5, it was shown that sodium oxides (a mixture of Na$_2$O and Na$_2$O$_2$) can be formed on MnO(100) by oxidizing a Na multilayer deposited on MnO(100) at 350 K. The reaction of water with surface sodium oxides will also be examined. Most importantly, it has also been shown that a surface exposing Na$_2$CO$_3$ islands on MnO(100) can be engineered to provide a model mixed oxide exposing Na$_2$CO$_3$/MnO interfaces, similar to the mechanical mixture of Na$_2$CO$_3$ and MnO thought to be important in the catalytic water splitting cycle proposed by Xu et al. [22]. It is our primary interest to test for hydrogen production from water on the engineered surface. Lastly, the active component for the hydrogen evolution under the conditions of our study is discussed.

6.2 Results and Discussion

6.2.1. Water adsorption on MnO(100) precovered with submonolayer oxidic Na

The surface was prepared by depositing 3 ML of Na on MnO(100) at 300 K followed by flashing to 500 K to desorb metallic Na. It has been found that the 500 K thermal treatment on a Na multilayer precovered MnO(100) surface yields about half a monolayer of the oxidic Na present on the surface.

Fig. 6.1 shows the TPD traces of D$_2$ (m/z = 4) and D$_2$O (m/z = 20) following a 0.5 L (1 L ≡ 1×10$^{-6}$ Torr·s) D$_2$O dose on the surface at 125 K. No hydrogen desorption is observed. Water desorbs primarily below 300 K with a peak maximum at 230 K, and with a higher temperature tail up to about 600 K, similar to the water TPD features from clean MnO(100) as described in Chapter 3, indicating that there is no strong interaction between water and oxidic Na on MnO(100).
Figure 6.1 TPD traces of D$_2$ (m/z = 4) and D$_2$O (m/z = 20) following 0.5 L D$_2$O adsorption on MnO(100) precovered with submonolayer oxidic Na.
6.2.2. Water adsorption on MnO(100) precovered with a Na multilayer (oxidic and metallic)

6.2.2.1. Water TPD from MnO(100) precovered with a Na multilayer

The surface was prepared by depositing 3 ML of Na on MnO(100) at 300 K, and exhibits both oxidic Na in the first monolayer and metallic Na islands as described in Chapter 2. Fig. 6.2 shows the TPD traces of D$_2$ (m/z = 4), D$_2$O (m/z = 20) and Na (m/z = 23) following a 0.5 L D$_2$O dose on the surface at 125 K. No water desorption is observed, but hydrogen desorption is observed at 210 K and 440 K. Na desorption is also observed at 425 K. No other Na-related products such as Na$_2$O (m/z = 62), NaOH (m/z = 40) or Na-O fragments (m/z = 39) are detected.

The absence of water desorption indicates a 100% conversion of water to hydrogen for a low water coverage. Given that no hydrogen evolution from water is observed in the presence of only oxidic Na on MnO(100) (Fig. 6.2), we conclude that water reacts with metallic Na on MnO(100) to produce hydrogen. Possible reactions include H$_2$O + 2Na → H$_2$ + Na$_2$O, 2H$_2$O + 2Na → H$_2$ + 2NaOH and 2H$_2$O + 2Na → 2H$_2$ + Na$_2$O$_2$, where water is reduced to hydrogen by metallic Na.

The origins of the two hydrogen desorption feature at 210 K and 440 K are not clear. Co-adsorption of water and Na on Ru(001) at 80 K [165] is known to form NaOH, which decomposes to give hydrogen between 350 K and 600 K. Therefore, the hydrogen desorption at 440 K might be related to the decomposition of NaOH, but no spectroscopic information is available about the nature of the surface intermediates associated with the two hydrogen desorption channels. The 425 K Na desorption is characteristic of the
**Figure 6.2** TPD traces of D$_2$ (m/z = 4), D$_2$O (m/z = 20) and Na (m/z = 23) following 0.5 L D$_2$O adsorption on MnO(100) precovered with a Na multilayer.
desorption of metallic Na as described in Chapter 2, indicating an incomplete oxidation of metallic Na for the small water dose.

6.2.2.2. CO₂ TPD characterization of the Na oxidation products by water

CO₂ was used as a probe molecule to characterize the oxidation products of metallic Na by water. A 3 ML Na-precovered MnO(100) surface was pre-exposed to a 0.5 L of D₂O at 125 K, and the TPD traces were collected following a 0.5 L ¹³CO₂ dose at 125 K as shown in Fig. 6.3. No water desorption is observed and hydrogen desorption is observed at 205 K and 440 K. A high temperature CO₂ desorption with a main feature at 805 K and a shoulder near 710 K are observed. No CO desorption is detected. Na desorption is observed at 430 K. No other Na-related products such as Na₂O (m/z = 62), NaOH (m/z = 40) or Na-O fragments (m/z = 39) are detected.

The absence of water desorption again demonstrates a 100% conversion of water to hydrogen at a low water coverage similar to that for water adsorption only (Fig. 6.2). The high temperature CO₂ desorption feature at 805 K is similar to the CO₂ TPD feature from a multilayer Na precovered MnO(100) after oxidation at 350 K as described in Chapter 5, and has been attributed to the decomposition of Na₂CO₃ formed by the interaction between CO₂ and Na₂O. This result indicates the presence of Na₂O after water adsorption on metallic Na, and is consistent with the suggestion in Section 6.2.2.1 that Na₂O is a likely byproduct of the reaction of water with metallic Na. The CO₂ desorption feature at 710 K is similar to that attributed to the Na₂CO₃ formed by CO₂ and Na₂O₂ as described in Chapter 5. However, it is also similar to that from chemisorbed CO₂ on metallic Na (735 K) as described in Chapter 2. Considering that metallic Na is characterized by a 430 K Na desorption feature, and also forms CO via a
**Figure 6.3** 0.5 L $^{13}\text{CO}_2$ TPD traces of $\text{D}_2$ (m/z = 4), $\text{D}_2\text{O}$ (m/z = 20), $^{13}\text{CO}_2$ (m/z = 45), $^{13}\text{CO}$ (m/z = 29) and Na (m/z = 23) on a Na multilayer precovered MnO(100) surface that is pre-exposed to 0.5 L D$_2$O.
disproportionation reaction from chemisorbed CO$_2$ on metallic Na, no CO desorption suggests the absence of chemisorbed CO$_2$ on metallic Na. Therefore, the 710 K CO$_2$ desorption feature likely arises from the interaction between CO$_2$ and Na$_2$O$_2$. This result is consistent with the suggestion in Section 6.2.2.1 that Na$_2$O$_2$ is a likely byproduct of the reaction of water with metallic Na. The absence of chemisorbed CO$_2$ on metallic Na while metallic Na is present on the surface suggests that water oxidizes surface Na of metallic Na islands while the inner core remains metallic and desorbs at 430 K. A similar incomplete oxidation of metallic Na has been seen for O$_2$ adsorption at 125 K as described in Chapter 5.

6.2.3. Water adsorption on MnO(100) precovered with sodium oxides

The surface was prepared by exposing a 3 ML Na precovered MnO(100) surface to 200 L of O$_2$ at 350 K. A mixture of Na$_2$O and Na$_2$O$_2$ is present on the surface as described in Chapter 5. Fig. 6.4 shows the TPD traces of D$_2$ (m/z = 4) and D$_2$O (m/z = 20) following a 0.5 L D$_2$O dose on the surface at 125 K. No hydrogen desorption is observed. A high temperature water desorption feature is observed at 655 K. Since it is generally observed that water desorption above room temperature in UHV is due to the recombinative desorption of dissociated water [111, 112], this desorption feature is attributed to the recombinative of dissociated water on sodium oxides.

6.2.4. Water adsorption on a surface exposing Na$_2$CO$_3$ islands on MnO(100)

A surface exposing Na$_2$CO$_3$ islands on MnO(100) has been engineered and characterized in Chapter 5 to model the mixed oxide Na$_2$CO$_3$/MnO for hydrogen evolution in the thermochemical water splitting cycle of Xu et al. [22]. The synthetic
Figure 6.4 TPD traces of D₂ (m/z = 4) and D₂O (m/z = 20) following 0.5 L D₂O adsorption on MnO(100) precovered with sodium oxides (a mixture of Na₂O and Na₂O₂).
procedure is as follows: (1) deposition of 3 ML of Na on MnO(100) at 300 K. This surface is known to expose oxidic Na in the first monolayer and metallic Na islands (Chapter 2). (2) oxidation of metallic Na islands with 200 L of O\textsubscript{2} at 350 K to form a mixture of Na\textsubscript{2}O and Na\textsubscript{2}O\textsubscript{2} on MnO(100) (Chapter 5). (3) formation of Na\textsubscript{2}CO\textsubscript{3} islands on MnO(100) by the reaction of 0.5 L of CO\textsubscript{2} with sodium oxides at 125 K (Chapter 5). (4) removal of oxidic Na in the first monolayer by heating to 600 K for 10 min to drive Na into the subsurface of MnO (Chapter 2). Note that this temperature is high enough to remove chemisorbed CO\textsubscript{2} from oxidic Na in the first monolayer (Chapter 2), but is lower than the temperature for the thermal decomposition of Na\textsubscript{2}CO\textsubscript{3} around 800 K (Chapter 5), and also lower than the temperature required for the solid state reaction of Na\textsubscript{2}O and MnO to form NaMnO\textsubscript{2} above 750 K (Chapter 5).

Fig. 6.5 shows the TPD traces of D\textsubscript{2} (m/z = 4), D\textsubscript{2}O (m/z = 20) and \textsuperscript{13}CO\textsubscript{2} (m/z = 45) from a 0.5 L D\textsubscript{2}O dose on the surface exposing Na\textsubscript{2}CO\textsubscript{3} islands on MnO(100). No hydrogen desorption is observed. Water desorption features are observed at 210 K, 410 K and 655 K, respectively. A high temperature CO\textsubscript{2} desorption feature is observed at 800 K. The water desorption feature at 205 K is similar to the desorption feature previously observed from water adsorption on terraces of MnO(100) as described in Chapter 3. The water desorption feature at 410 K fits the characteristics of bicarbonate formation from water and CO\textsubscript{2} near surface defects of MnO(100) as described in Chapter 3. Since any \textsuperscript{13}CO\textsubscript{2} dosed to form Na\textsubscript{2}CO\textsubscript{3} in step (3) of the synthetic procedure should be depleted from the partially exposed MnO(100) after the 600 K thermal treatment in step (4), the bicarbonate is likely to be formed from water and background CO\textsubscript{2} (m/z = 44), which explains the absence of \textsuperscript{13}CO\textsubscript{2} (m/z = 45) desorption around 400 K. The water desorption
Figure 6.5 TPD traces of $\text{D}_2$ (m/z = 4), $\text{D}_2\text{O}$ (m/z = 20) and $^{13}\text{CO}_2$ (m/z = 45) following 0.5 L $\text{D}_2\text{O}$ adsorption on the engineered surface exposing $\text{Na}_2\text{CO}_3$ islands on MnO.
feature at 655 K has been seen from water adsorption on sodium oxides (Fig. 6.4), and has attributed to the recombination of dissociated water on sodium oxides, indicating that a portion of sodium oxides remain on the surface after the low CO$_2$ exposure. The high temperature CO$_2$ desorption feature at 800 K is similar to that from the decomposition of Na$_2$CO$_3$ at 800 K as described in Chapter 5, and is attributed to the decomposition of Na$_2$CO$_3$ islands on the engineered surface. Therefore, we have tested the reaction of water with an engineered surface exposing Na$_2$CO$_3$ islands on MnO(100) used to model the mixed oxide Na$_2$CO$_3$/MnO for hydrogen evolution in the thermochemical water splitting cycle of Xu et al. [22], but no hydrogen evolution from water is observed.

6.2.5. Insights into the reaction mechanism of hydrogen evolution

Some similarities are found in our model system and the catalytic system of Xu et al. [22]. In the hydrogen evolution steps of Xu et al. [22], Na$_2$CO$_3$ reacts with MnO in the presence of water to form NaMnO$_2$ and CO$_2$, while water splits to produce hydrogen. In our system, we have observed the decomposition of Na$_2$CO$_3$ to give CO$_2$ in the presence of water in this chapter, similar to the release of CO$_2$ reported in Xu et al. [22], but NaMnO$_2$ is formed through a solid state reaction between Na$_2$O and MnO (Chapter 5). In our case, the presence of water is not required for the solid state reaction, but the release of CO$_2$ from Na$_2$CO$_3$ could yield Na$_2$O in the catalytic system as a reaction intermediate.

However, we have engineered a surface exposing Na$_2$CO$_3$ islands on MnO(100) in Chapter 5 to model the mixed oxide Na$_2$CO$_3$/MnO for hydrogen evolution in the thermochemical water splitting cycle of Xu et al. [22], but no hydrogen evolution from water is observed on our model surface. This contrasts with the proposal by Xu et al. [22]
that Na$^+$ in Na$_2$CO$_3$ is the active component for water splitting. Two possible explanations are postulated. One possibility is that our model system fails to function like the true catalytic system. The reasons are likely associated with the very different operation conditions for the two systems. In the hydrogen evolution steps of Xu et al. [22], a mixed oxide Na$_2$CO$_3$/MnO catalyst is heated to 850 °C (1123 K), and water vapor is introduced by flowing through the catalyst bed in a constant flux. In contrast, under the conditions of our study, a low coverage of water (0.5 L) is introduced and adsorbed on the surface exposing Na$_2$CO$_3$ islands and MnO(100) at a very low temperature (125 K). It has been found in TPD (Fig. 6.5) that all the adsorbed water desorbs from the surface below 800 K, and all the Na$_2$CO$_3$ decomposes to give CO$_2$ below 900 K. At the working temperature of 850 °C (1123 K) for the water splitting catalysis of Xu et al. [22], water and Na$_2$CO$_3$ are the reactants for the hydrogen evolution, but in our TPD study these reactants desorb (water) and decompose (Na$_2$CO$_3$) before we reach the reaction temperature used for catalytic system. Therefore, it is likely that the activation barrier for the kinetically important steps in the water splitting cycle of Xu et al. [22] exceeds those for the desorption of water and the decomposition of Na$_2$CO$_3$ in our TPD experiments.

There is a second possible explanation. In this chapter, hydrogen evolution from water is only observed in the presence of metallic Na on MnO(100). Therefore, we conclude that metallic Na is the active component for the hydrogen evolution from water under the conditions of our study. This result is not surprising, because water is known to react rapidly with Na metal to produce hydrogen gas. In the thermochemical water splitting cycle of Xu et al. [22], the shuttling of Na into and out of the manganese oxides is thought to be the key process for enabling the Mn$^{2+}$/Mn$^{3+}$ redox cycle responsible for
hydrogen and oxygen evolution. It is possible that, at the working temperature of 850 °C (1123 K) for the water splitting catalysis [22], a transient form of metallic Na is present during the solid state transformations associated with the shuttling of Na between different phases. If such is the case, metallic Na could be the active component in the catalytic system of Xu et al. [22]. Combining results in this study, a multi-step process for hydrogen evolution from water can be postulated as follows:

\[ Na_2CO_3 \rightarrow Na_2O + CO_2 \] (Chapter 5)

\[ 2Na_2O + 2MnO \rightarrow 2NaMnO_2 + 2Na \] (Chapter 5)

\[ 2Na + H_2O \rightarrow Na_2O + H_2 \] (Chapter 6)

where metallic Na is produced in the process and reacts with water to produce hydrogen. This multi-step process yields a net reaction equation that is the same as the reaction equation of step 2 in the water splitting cycle of Xu et al. [22].

6.3 Conclusion

Water reacts with metallic Na on MnO(100) to produce hydrogen. No hydrogen evolution from water is observed on a surface exposing Na₂CO₃ islands on MnO(100) which is used to model the mixed oxide Na₂CO₃/MnO for hydrogen evolution in the thermochemical water splitting cycle of Xu et al. [22]. Metallic Na is the active component for the hydrogen evolution from water under the conditions of our study.
Chapter 7

Conclusions and Recommendations for Future Work

7.1 Conclusions

In this UHV surface science study the interactions of Na, O\textsubscript{2}, CO\textsubscript{2} and water on MnO(100) have been investigated. The work was undertaken in an effort to understand the fundamentals of the reaction mechanism for hydrogen evolution in the thermochemical water splitting cycle of Xu et al. [22].

7.1.1. The interaction between Na and MnO(100)

Na adsorption on the MnO(100) surface follows the Stranski-Krastanov (SK) growth mode with two forms of Na identified as described in Chapter 2. Up to 1 ML Na coverage, Na is randomly distributed on the MnO(100) surface before the completion of the monolayer and interacts strongly with the MnO substrate, binding in an oxidic form. This form of Na is irreversibly-adsorbed and diffuses into the MnO bulk at elevated temperatures above 500 K. For Na coverages above 1 ML, metallic Na islands nucleate and grow on top of the Na monolayer. Metallic Na desorbs from the surface at 430 K.

7.1.2. The formation of NaMnO\textsubscript{2} and the redox cycle of Mn

The formation of a NaMnO\textsubscript{2}-like surface (Mn\textsuperscript{3+}) is described in Chapter 4 by annealing a MnO(100) (Mn\textsuperscript{2+}) surface precovered with a high coverage of metallic Na (11.5 ML) in O\textsubscript{2} at elevated temperatures (675 K) and subsequently flashing to 1000 K. In Chapter 5, a NaMnO\textsubscript{2}-like surface compound is also formed by a solid state reaction
between Na$_2$O and the MnO(100) substrate above 750 K. NaMnO$_2$ formed via both approaches thermally decomposes above 850 K to give surfaces similar to MnO(100). Thus a redox cycle of Mn between 2+ (MnO) and 3+ (NaMnO$_2$) is achieved, similar to the redox of Mn in the thermochemical water splitting cycle of Xu et al. [22].

7.1.3. The formation of Na$_2$CO$_3$

In Chapter 5, Na$_2$O and Na$_2$O$_2$ are formed from the oxidation of metallic Na islands by O$_2$ at 350 K on MnO(100), and Na$_2$CO$_3$ is formed by the strong interaction between CO$_2$ and both Na$_2$O and Na$_2$O$_2$. The decomposition of Na$_2$CO$_3$ to give CO$_2$ around 800 K along with the solid state reaction of Na$_2$O and MnO(100) to form NaMnO$_2$ above 750 K (Section 7.1.2) is similar to the reaction of Na$_2$CO$_3$ and MnO to form NaMnO$_2$ and CO$_2$ in the presence of water in the hydrogen evolution steps of Xu et al. [22].

7.1.4. The engineered surface exposing Na$_2$CO$_3$ islands on MnO(100)

A surface exposing Na$_2$CO$_3$ islands on MnO(100) has been engineered in Chapter 5 to model the complex mixed oxide Na$_2$CO$_3$/MnO for hydrogen evolution in the thermochemical water splitting cycle of Xu et al. [22].

7.1.5. The reaction of water with various surfaces

The reaction of water with several surfaces have been studied to determine if any single components or combinations of materials can give rise to hydrogen evolution from water in a traditional UHV surface science environment. No hydrogen evolution from water occurs from MnO(100), Mn$_3$O$_4$ and NaMnO$_2$ surfaces which appear in the catalytic
cycle of Xu et al. [22], and is consistent with the suggestions from Xu et al. [22] that these materials do not individually promote water splitting.

Na$_2$CO$_3$ is thought to be critical for the hydrogen evolution in the thermochemical water splitting cycle of Xu et al. [22]. Surfaces combining MnO and Na$_2$CO$_3$, as well as surfaces combining MnO and components of Na$_2$CO$_3$ (e.g. Na$_2$O and Na) have also been tested for hydrogen production from water. Water reacts with metallic Na on MnO(100) to produce hydrogen and sodium oxides. No hydrogen evolution from water is observed on either oxidic Na in the first monolayer on MnO(100) or sodium oxides on MnO(100). Most importantly, no hydrogen evolution from water is observed on the engineered surface exposing Na$_2$CO$_3$ islands on MnO(100) used to model the mixed oxide Na$_2$CO$_3$/MnO used in the thermochemical water splitting cycle of Xu et al. [22] under the conditions of our study.

7.1.6. Insights into the reaction mechanism of hydrogen evolution from water

Hydrogen evolution from water is only observed in the presence of metallic Na on MnO(100). Therefore, metallic Na is the active component for the hydrogen evolution from water under the conditions of our study. It is possible that at the working temperature of 850 °C (1123 K) for the water splitting catalysis [22] a transient form of metallic Na not observed by Xu et al. is present during the solid state transformations associated with the shuttling of Na between different phases. If such is the case, metallic Na could also be the active component in the catalytic system of Xu et al. [22].

The lack of hydrogen evolution from water on the engineered model surface exposing Na$_2$CO$_3$ islands on MnO(100) contrasts with the proposal by Xu et al. [22] that Na$^+$ in Na$_2$CO$_3$ is the active component for water splitting in the presence of MnO. If this
is the case, our model system fails to function like the true catalytic system, and the reasons are most probably associated with the very different operation conditions for the two systems. It is likely that the activation barrier for the kinetically important steps for water splitting on the catalyst of Xu et al. [22] exceeds those for the desorption of water and the decomposition of Na$_2$CO$_3$ in our TPD experiments.

7.2 Recommendations for Future Work

7.2.1. XPS characterization and DFT calculations of CO$_2$ and water adsorption on MnO(100)

In Chapter 3, CO$_2$ and water adsorption on MnO(100) have been investigated. Experimental results indicate that CO$_2$ adsorbs molecularly on both terraces and defects of MnO(100), while water adsorbs molecularly on terraces and dissociatively on surfaces defects. Bicarbonate is suggested to form from adsorbed CO$_2$ and water near surface defects of MnO(100).

DFT calculations can provide information of the geometric and electronic structures of adsorbed CO$_2$ and water molecules on MnO(100) to justify the interpretation of experimental results. Preliminary DFT calculations in our group give values of heats of adsorption of CO$_2$ matching well with the experimental activation energy of desorption of molecular CO$_2$ from terrace sites. However, DFT predicts a significantly greater heat of adsorption at surface steps than observed experimentally from defects. Therefore, other types of defect sites such as cation and anion vacancies should be explored computationally, and the nature of surface defect sites on MnO(100) may be identified.
DFT calculations can also be applied to the adsorbed water on terraces and defects. Calculated values of the heat of adsorption of molecular water on terrace sites can be compared to the experimental activation energy of desorption of water from terrace sites. Stable structures of adsorbed water near surface defect sites obtained from DFT calculations can be used to provide information about the dissociation of water on defects.

In addition, DFT calculations can be performed to probe stable structures of adsorbed CO$_2$ and water/hydroxyl combinations near surface defect sites attributed to the formation of bicarbonate species assigned on the basis of TPD data alone.

7.2.2. C 1s XPS characterization of the Na$_2$CO$_3$ formation

In Chapter 5, CO$_2$ TPD results indicate that Na$_2$CO$_3$ is formed by the interaction between CO$_2$ and sodium oxides on MnO(100). C 1s XPS can be used to characterize the formation of carbonate. It has been reported that the formation of carbonate from the interaction between CO$_2$ and MgO(100) gives a characteristic C 1s XPS feature around 289 eV [110, 166]. However the C 1s XPS spectra acquired in this work with a Mg radiation source overlaps with intense features of Na KLL Auger lines, thus no information of the carbonate formation is obtained from the C 1s XPS. Utilizing an Al source, the C 1s and Na KLL spectra can be well separated, since the higher incident photon energy from the Al x-ray source results in Na KLL Auger binding energies shifting to higher values but no change in C 1s binding energy. Therefore the C 1s XPS characterization may provide evidence to justify the assignment of carbonate formation.
7.2.3. XPS characterization of hydrogen evolution from water on metallic Na

In Chapter 6, water reacts with metallic Na on MnO(100) to produce hydrogen in TPD at two different temperatures. However, the nature of the surface intermediates associated with the two hydrogen desorption channels is not clear. During the water adsorption studies performed in this work, XPS was not available in our laboratory. However, O 1s XPS can be used to characterize changes in chemical state of oxygen to justify the presence of molecular water, hydroxyl groups or oxygen anions. Peng and Barteau [167] studied water adsorption on MgO(100) and reported an O 1s XPS binding energy of 533.1 eV attributed to surface hydroxyl groups, which is 2.1 eV higher than that form the lattice oxygen in MgO. Similar 1.8 - 2.4 eV increase of O 1s binding energy from lattice oxygen in oxide to surface hydroxyl groups has been reported on MnO(100) [126] and more on MgO(100) [168, 169]. In contrast, molecularly adsorbed water is expected to give O 1s features at about 4 eV above the O 1s feature from oxides [126, 167-169]. Similarly, Na 1s and Na KLL XPS can be used to characterize changes in chemical state of Na to justify the presence of metallic Na and sodium oxides. A 0.7 eV binding energy increase in Na 1s [64, 77, 98] and 4.5 eV in Na KLL [98] are reported for the oxidation of metallic Na to Na₂O. Thus, XPS experiments following water adsorption may help identify the surface intermediates associated with the two hydrogen desorption channels, and provide information on the elementary steps in the hydrogen evolution from water on metallic Na.
References


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Appendix A. XPS atomic sensitivity factors

The ratio of empirical XPS atomic sensitivity factors was estimated by

\[
\frac{S_1}{S_2} \approx \frac{\sigma_1 \lambda_1 / KE_1}{\sigma_2 \lambda_2 / KE_2}
\]

as described elsewhere [45, 46], where \( S_i \) is the sensitivity factor for element \( i \), \( \sigma \) is the photoionization cross section of the element core level, \( \lambda \) is the inelastic mean free path of the photoemitted electron, and \( KE \) is the kinetic energy of the photoemitted electron and corrects for the \( 1/E \) dependence of the analyzer transmission function. The atomic photoionization cross sections were found in published data calculated from a Hartree-Fock-Slater one-electron central potential model [47]. The inelastic mean free paths were estimated using a predictive formula (TPP-2M equation [48, 49]) in the NIST Electron Inelastic-Mean-Free-Path Database [50] and depend on the number of valence electrons per molecule \( N_v \), band gap energy \( E_g \) (eV), density \( \rho \) (g/cm\(^3\)) and kinetic energy \( KE \) (eV).

1. MnO

Table A.1 Predicted inelastic mean free paths (MnO).

<table>
<thead>
<tr>
<th>( N_v )</th>
<th>( E_g ) (eV)</th>
<th>( \rho ) (g/cm(^3))</th>
<th>( \lambda ) (Å)</th>
<th>KE (eV)</th>
<th>723.5 eV (O 1s)</th>
<th>612.5 eV (Mn 2p)</th>
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<tr>
<td>13</td>
<td>3.9 [170]</td>
<td>5.37 [171]</td>
<td>15.47</td>
<td>13.73</td>
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<td></td>
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</tbody>
</table>

Table A.2 Estimated ratio of XPS atomic sensitivity factors (MnO).

<table>
<thead>
<tr>
<th></th>
<th>( \sigma )</th>
<th>( \lambda ) (Å)</th>
<th>KE (eV)</th>
<th>( S_O/S_{Mn} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>0.063 [47]</td>
<td>15.47</td>
<td>723.5</td>
<td>0.20</td>
</tr>
<tr>
<td>Mn 2p</td>
<td>0.3011 [47]</td>
<td>13.73</td>
<td>612.5</td>
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</table>
2. NaMnO₂

Table A.3 Density of NaMnO₂.

<table>
<thead>
<tr>
<th>lattice constants (Å)</th>
<th>volume per unit cell (cm³)</th>
<th>mass per unit cell (g)</th>
<th>density ρ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a=5.63, b=2.86, c=5.77</td>
<td>8.41×10⁻²³</td>
<td>3.65×10⁻²²</td>
<td>4.34</td>
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</table>

Table A.4 Predicted inelastic mean free paths (NaMnO₂).

<table>
<thead>
<tr>
<th>Nv</th>
<th>E_g (eV)</th>
<th>ρ (g/cm³)</th>
<th>KE (eV)</th>
<th>λ (Å)</th>
<th>723.5 eV (O 1s)</th>
<th>611.7 eV (Mn 2p)</th>
<th>182.4 eV (Na 1s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.8* [173]</td>
<td>4.34</td>
<td>λ (Å)</td>
<td>16.15</td>
<td>14.30</td>
<td>6.74</td>
<td></td>
</tr>
</tbody>
</table>

* no experimental band gap data is available for NaMnO₂ so a reported value for sodium birnessite-type MnO₂ (NaMnO₂·nH₂O) is adopted.

Table A.5 Estimated ratios of XPS atomic sensitivity factors (NaMnO₂).

<table>
<thead>
<tr>
<th>KE (eV)</th>
<th>O 1s</th>
<th>Mn 2p</th>
<th>Na 1s</th>
</tr>
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<tbody>
<tr>
<td>723.5</td>
<td>0.063 [47]</td>
<td>0.3011 [47]</td>
<td>0.1781 [47]</td>
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<tr>
<td>611.7</td>
<td>0.20</td>
<td>0.21</td>
<td>0.21</td>
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<tr>
<td>182.4</td>
<td>0.20</td>
<td>0.21</td>
<td>0.21</td>
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