

Growth and vibrational properties of MnO_x thin films on Rh(111)

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ABSTRACT

The growth, structures, and vibrational properties of ultrathin manganese oxide films on Rh(111) had been investigated using high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), low energy ion scattering spectroscopy (LEIS) and Auger electron spectroscopy (AES). MnO_x grew in a layer-by-layer fashion on the Rh(111) surface. HREELS phonon features and XPS binding energies showed that an O–Mn–O– like tri-layer formed initially. Which was stable on the Rh(111) surface with MnO_x coverage less than one monolayer. At above one monolayer, Mn_3O_4 was preferred as indicated from a four-phonon feature peaked at 13.3, 39, 68 and 83 meV in HREELS. Higher temperature oxidation and annealing were found to improve the long-range order of the MnO_x films.

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1. Introduction

Manganese oxides have been extensively studied due to their wide range applications in catalysis, electrochemistry, ion-exchange materials, magnetite, batteries, and other areas [1–14]. Manganese oxides naturally crystallized into MnO , Mn_3O_4 , Mn_2O_3 and MnO_2 . Among them, Mn_3O_4 , Mn_2O_3 and MnO_2 are effective catalysts used to clear up NO_x , CO and volatile organic compounds (VOCs) [1–6], common electrode materials [7–10], and soft magnetic materials [11]. MnO was found to be an effective additive to improve the selectivity of C_2 oxygenates from CO hydrogenation on Rh-base catalysts [12–14]. But the roles of MnO were still unclear. It was proposed that CO adsorbed on Rh– MnO_x interface with a tilted configuration, which promoted the dissociation of CO [12,13]. The interface species of $\text{Rh}^{\delta+}$ might favor the CO insertion for C_2 formation [14].

Most studies of manganese oxides have been focused on the bulk or powder samples, few on thin oxide film. To fully understand the chemical and physical properties of manganese oxides, detailed studies using full function modern surface science techniques are required. However, most metal oxides are electrical insulators, which restrict the application of surface science techniques owing to a surface charging problem during measurements. Thin oxide films growing on various metal substrates provide effective ways to solve the surface charging problem. Manganese oxide thin films, mainly MnO_x , have been grown on Ag(001) [15], Pd(100) [16,17], Pt(111) [18] and Rh(100) [19]. Mn_3O_4 was known to have a normal spinel structure [4]. However,

well-defined Mn_3O_4 thin film was hard to be synthesized, due to phase transformation and instability of the polar surfaces. The later led to that the (001) oriented facet was the mainly exposing surface for Mn_3O_4 thin films [20–22]. However, extensive approaching to the structural stabilization of Mn_3O_4 thin films was still missing in the literature.

In this paper we focused on the preparation and characterization of thin MnO_x films (0–3 ML) on a Rh(111) surface. Layer-by-layer growth and a phase transition of O–Mn–O– tri-layer like monolayer film to Mn_3O_4 were identified. Such surfaces can serve as model catalysts for detail studies of the promotion effects of MnO_x on Rh for C_2 -oxygenates synthesis from syngas, as well as the reaction mechanism.

2. Experiments

The experiments were carried in two separate ultrahigh vacuum (UHV) chambers, both with a typical base pressure of $<5 \times 10^{-10}$ Torr. One is equipped with a high-resolution-electron energy loss spectroscopy (HREELS, LK-5000), an Auger electron spectroscopy (AES), and a low-energy electron diffraction (LEED). The HREELS measurements were performed in a specular reflection geometry $\Theta_{\text{in}} = \Theta_{\text{out}} = 35^\circ$ with a primary energy of 7.254 eV and a typical resolution of ~ 2 meV. The X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectroscopy (LEIS) (Thermo Multilab 2000) were carried out in the second chamber. Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV) and a pass energy of 50 eV were used. The binding energy (BE) of the XPS spectrometer was calibrated with respect to the pure bulk Rh (3d5/2 BE = 307.0 eV) for each spectrum.

The Rh(111) crystal (purchased from Princeton Scientific Corp.) was cleaned by repeated cycles of Ar^+ sputtering following by a subsequent oxidation at 700 K in 1×10^{-7} Torr O_2 , and annealing at 1100 K in UHV.

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The cleanliness of the surface was confirmed by AES and LEED, or by XPS. In the HREELS chamber, the sample can be heated up to 2000 K by electron bombardment and cooled down to 100 K using a liquid nitrogen trap. The sample temperature was monitored by a C-type thermocouple (W-5%Re/W-26%Re/W) spot-welded to the back supporting Ta plate. In the XPS chamber, the sample was mounted on a Ta wire that can be heated up to 1200 K resistively. A C-type thermocouple was spot welded to the edge of the Rh(111) disk. Manganese was evaporated from a piece of manganese (Alfa 99.95%) wrapped tightly by a Ta wire and was thoroughly degassed prior to deposit onto the surface. The manganese oxide films were prepared by deposition of metallic manganese in ultra-high vacuum (UHV) onto Rh(111) at room temperature, following an oxidization at 600–800 K and cooling down to room temperature in 1×10^{-7} Torr O_2 . The coverage of manganese oxide was calibrated by AES and XPS in which breakpoints were observed by plotting the Mn/Rh AES or XPS ratio as a function of the deposition time. The coverage of one monolayer (ML) was defined from the AES and XPS breakpoint, in which a single atomic layer of oxide film was supposed to cover the whole substrate surface. This was also confirmed by LEIS and by HREELS using CO as a probe. High purity CO (Hong Kong Specialty Gases Co., Ltd.) was further purified by a liquid nitrogen trap before it was introduced to the chamber and the sample was kept at 100 K by liquid nitrogen during CO adsorption experiment.

3. Results and discussion

MnO_x thin films were grown by deposition of Mn onto a Rh(111) surface following by a subsequence oxidation in 1×10^{-7} Torr O_2 at 723 K. The XPS ratio of $Mn2p_{3/2}$ to $Rh3d_{5/2}$ as a function of Mn deposition time was displayed in Fig. 1. Three break-points were evidenced at 18, 34 and 51 min, respectively. According to the thin film growth modes [23], such XPS ratio varying as a function of deposition time was characteristic of a layer-by-layer growth mode of MnO_x on Rh(111). Thus, the amount of MnO_x achieved at the deposition time of 18 min can be defined as one monolayer (1 ML), which corresponds to a full cover of the Rh(111) surface by a one atomic layer thick of MnO_x . Such breakpoints of Mn/Rh ratio as a function of deposition time were also observed in AES measurements in the HREELS chamber. The full cover of the Rh(111) surface by MnO_x at the first breakpoint was confirmed by both LEIS and HREELS using CO as a probe (detail will be discussed later).

Fig. 2 showed XPS spectra of $Mn2p$ and $O1s$ core levels during the growth of manganese oxide thin films from submonolayer to multilayer. The $Mn2p_{3/2}$ appeared a broad feature peaked at 641.5–641.7 eV, a value typical for Mn^{2+} and Mn^{3+} as shown in Table 1 [1,2,24,25]. A small blue-shift of 0.2 eV was observed from the submonolayer to multilayer. The broad $Mn2p$ peaks with complex shapes had been

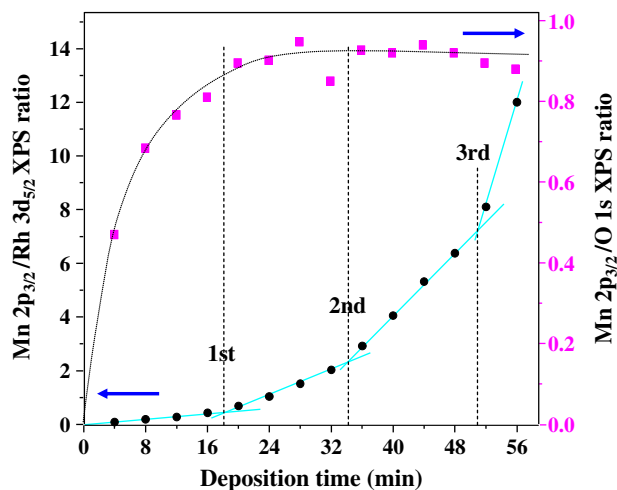


Fig. 1. $Mn2p_{3/2}/Rh3d_{5/2}$ and $Mn2p_{3/2}/O1s$ XPS ratios versus deposition time.

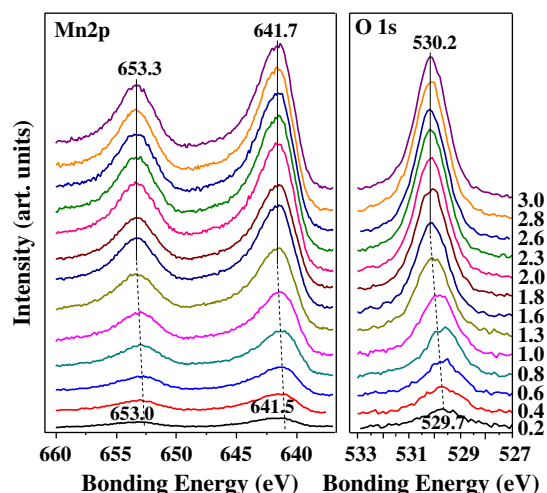


Fig. 2. XPS spectra for $Mn2p$ and $O1s$ at different MnO_x coverages. MnO_x coverages were indicated at the right side of the figure.

contributed to the multiple splitting, correlation and configuration interaction effects in the final state [26]. The spin-orbit splitting of $Mn2p_{3/2}$ and $Mn2p_{1/2}$ was almost constant at 11.6 eV for various Mn coverages, which is located between 11.25 and 11.7 eV for metallic Mn and MnO_2 , respectively. Concurrently, a small blue shift of $O1s$ core level from 529.7 to 530.2 eV was observed. Based on the above observation and discussion, it can tentatively be assigned the broad $Mn2p$ feature to Mn^{2+} or Mn^{3+} . Note that a small variation of about 1 eV for $Mn2p$ from Mn^{2+} to Mn^{4+} and the broad features made the assignment of the Mn valence state difficult. And the case could be even worse if the MnO_x was presented in mixed chemical states.

The XPS ratio of $Mn2p_{3/2}$ to $O1s$ was also plotted as a function of the deposition time in Fig. 1. At submonolayer (deposition time below 18 min), the ratio increased quickly to a value of 0.9 which was almost constant at 0.9 for the MnO_x coverage higher than 1 ML. Note that the lower XPS $Mn2p_{3/2}/O1s$ ratio in submonolayer should result from the contribution of chemisorbed oxygen on Rh(111). This was evidenced from the appearance of Rh–O phonon in HREELS and a (2×2) LEED pattern after exposing the clean Rh(111) surface to oxygen (see Figs. 3 and 4).

The HREELS spectra for the various coverages of MnO_x were displayed in Fig. 3(a). The clean Rh(111) was exposed to a certain amount of oxygen at room temperature before taking a spectrum for reducing possible contamination by picking up the residue gas in UHV. A single loss feature peaked at 68.2 meV was observed. This feature can be assigned to a Rh–O phonon of surface chemisorbed oxygen [27]. Upon depositing MnO_x onto Rh(111), additional loss features peaked at 47, 74 and 88 meV appeared. As the MnO_x coverage increased, the loss peak at 74 meV continuously shifts to higher loss energy with its intensity and the 47 meV one increased synchronously, while the Rh–O peak of surface chemisorbed oxygen decreased and faded away at 1 ML. At 1 ML, there were only two loss peaks at 47 and 81 meV observed. Two loss features of 48 and 65 meV were observed for a 20 ML $MnO(001)$ thin film on Pd(100) [21,28]. However, single phonon loss of 44 meV and 70 meV was observed for the submonolayer MnO_x on

Table 1
XPS data for bulk and nanocrystals MnO_x from Refs. [2,4,24,25].

Sample	Peak position (eV)			Mn/O atomic ratio
	$Mn2p_{3/2}$	$Mn2p_{1/2}$	$O1s$	
MnO	641.2	653.0	531.2	1.08
Mn_3O_4	641.7	653.4	529.8	0.77
Mn_2O_3	641.8	654.1	529.7	0.60
MnO_2	642.1	653.5	529.9	0.51

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