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Article

Atomic structures and electronic properties of Cr-doped ZnO(10 $\bar{1}$ 0) surfaces

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ABSTRACT

An integrated approach combining scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) is used to investigate the atomic structures and electronic properties of Cr-doped ZnO(10 $\bar{1}$ 0) surfaces. When deposited at 300 K, Cr at low surface coverage (< 0.1 ML) appeared either as isolated atoms on the surface terrace of ZnO(10 $\bar{1}$ 0) or substituting Zn atoms in the ZnO lattice. Their structural models could be identified from atomic-resolution STM images and their oxidation states were found as Cr³⁺ based on XPS measurements. Rectangular islands nucleated at step edges along the [0001] direction could also be observed during the initial growth of Cr at 300 K and were assigned as Cr islands. The density of Cr islands as well as their average size increased with the increasing of Cr surface loading. Thermal treatments at above 600 K could facilitate the decomposition of Cr islands and the re-dispersion of Cr atoms into the ZnO lattice, indicating a strong interaction between Cr and ZnO. The adsorption of CO at 78 K showed no preferential adsorption at Cr³⁺ sites embedded in the surface lattice of ZnO. However, the re-dispersion of Cr atoms into the ZnO bulk at above 600 K could induce a significant upward band bending, causing a negative shift of core level XPS peaks of Zn 2p and O 1s by ~0.5–0.7 eV. Our study has thus constructed a model catalyst for Cr-doped ZnO and provided atomic insight for understanding ZnO-based catalysts.

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1. Introduction

ZnO is widely used for a number of technical applications, such as electronics, optics and catalysis, and for this reason, one of the most extensively studied metal oxides in fundamental research. In catalysis, ZnO-based catalysts were widely explored for processes, such as methanol synthesis [1,2], syngas (CO/H₂) conversion to light olefins [3,4] and water-gas shift [5].

To improve the reactivity of ZnO for catalytic reactions such as CO hydrogenation [4], developing ZnO-based oxides or doping ZnO has been employed as an efficient strategy in recent research efforts. For instance, Jiao et al. reported an OX-ZEO process using a ZnCrO_x-zeolite composite catalyst, that could break the limit of ASF distribution for syngas conversion [3]. Further developments based on ZnMO_x-zeolite (M = Cr [3,6,7], Zr [8,9], Ga [10]) have attracted increasing attention on the studies of

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ZnO-based mixed oxides and demanded model studies to understand the atomic structures of these mixed oxide surfaces, as well as their catalytic nature.

CO activation on the ZnCrO_x catalyst is considered as a key elementary step for the OX-ZEO process and recent studies have also suggested the transformation of ZnCrO_x into the non-stoichiometric spinel ZnCr_2O_4 with excess of ZnO during syngas conversion [3,7]. Nevertheless, elucidating the active site structures of ZnCrO_x surfaces has remained a difficult challenge in syngas conversion catalysis, which hampered further understanding on the reaction mechanism at the molecular level. To access the atomic-scale properties of oxide catalysts, fundamental studies over well-defined oxide model catalysts have played an essential role to understand the atomic structures of oxide surfaces, as well as the catalytic reaction mechanisms occurring on these surfaces. Particularly, a number of metal oxide single crystals, including TiO_2 [11–13], ZnO [14,15] and CeO_2 [16–18], have been studied extensively by surface science techniques to understand their surface chemistry at the molecular level. For instance, surface structures and adsorption properties of low-index surfaces of ZnO have been explored using scanning tunneling microscopy (STM) and vibrational spectroscopies [19,20]. Here, we propose to use single-crystal ZnO surfaces to investigate the effect of Cr doping, and on this basis to develop a Cr-doped ZnO model catalytic system for understanding ZnCrO_x catalysts. Indeed, doping has been widely used as an effective approach to tune the electronic properties and chemical reactivity of oxide materials [21–23]. For instance, Bechstein et al. studied the surface of rutile $\text{TiO}_2(110)$ doped with 2%–3% Cr using noncontact atomic force microscopy [24]. They observed the presence of added Cr_2O_3 stripes on surface Ti rows, enhancing the formation of surface oxygen vacancies.

In this paper, we studied the growth, structure and electronic properties of Cr on $\text{ZnO}(10\bar{1}0)$ at the atomic scale, using the combination of low temperature STM (LT-STM) and X-ray photoelectron spectroscopy (XPS). The structural characters and electronic properties of Cr atoms on ZnO were studied at varying surface coverages, which exhibited growth behavior drastically different from the growth of other metals on ZnO reported previously. Our study has thus provided a model system and atomic insight for further studies of CrO_x/ZnO catalysts.

2. Experimental

STM experiments were performed on an ultrahigh vacuum (UHV) system consisting of LT-STM (Createc) chamber with pressure of 4×10^{-11} mbar and preparation chamber. STM images were obtained with an electrochemical-etched tungsten tip at 78 K. All STM images were acquired in constant-current mode and processed with SPIP software (Imagemet, Denmark).

$\text{ZnO}(10\bar{1}0)$ single crystal (Mateck) was cleaned by cycles of Ar^+ bombardment (1.0 kV, 10 μA) and subsequent annealing in UHV at 1100 K. After high temperature treatment, the conductivity of ZnO was always unsatisfying for STM measurements. Interstitial H accounts for the conductivity of ZnO [25,26]. Thus,

to increase the conductivity, $\text{ZnO}(10\bar{1}0)$ was treated in 5×10^{-8} mbar H_2 at 400 K for 5 min, and then annealed under UHV for 30 seconds to remove possible H species adsorbed on surface. Before deposition, evaporators were outgassed at temperature higher than evaporation temperature to ensure no contamination was introduced. Metallic Cr was thermally deposited on a clean $\text{ZnO}(10\bar{1}0)$ surface under UHV conditions. Cu was deposited under similar condition. CO gas was purified through a liquid nitrogen cooling trap for at least 30 mins before introduction into chambers.

To investigate surface electronic states of the $\text{Cr}/\text{ZnO}(10\bar{1}0)$, XPS experiments were carried out at the Catalysis and Surface Science end-station at BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The beamline offers soft-X ray from 20–600 eV and Al K_α X-ray (1486.6 eV) as excitation sources. All XPS spectra were acquired at 300 K under UHV condition. Photon energies of 600 eV for O 1s and 120 eV for Cr 3p were used. Zn 2p and Cr 2p were detected with Al K_α source. Binding energies (BEs) were referenced to Au 4f_{7/2} at 84.0 eV determined from an Au foil.

3. Results and discussion

3.1. Surface and defect structure of $\text{ZnO}(10\bar{1}0)$

As the energetically most stable surface of ZnO, $\text{ZnO}(10\bar{1}0)$ has been studied extensively using surface science techniques. While the geometric and electronic structures of $\text{ZnO}(10\bar{1}0)$ have been documented in the literature, the defect structures on the $\text{ZnO}(10\bar{1}0)$ surface has not been clear at the atomic level. Fig. 1 showed STM images of a clean $\text{ZnO}(10\bar{1}0)$ surface, with well-defined flat terraces and the step height of 0.28 nm. The bright rows (Fig. 1(a)) along $[1\bar{2}10]$ direction are assigned to Zn atoms, according to the literature [27]. When Zn atoms were resolved atomically as protrusions, the rectangular unit cell could be visualized with vectors along the $[0001]$ and $[1210]$ directions and unit cell lengths at 0.52 and 0.32 nm, respectively.

Surface defects of $\text{ZnO}(10\bar{1}0)$ have been less studied, since ZnO is known to be difficult to reduce even after high-temperature annealing in UHV [28]. Figs. 1(b) and (c) showed two types of dark depressions in the bright Zn rows, which could be point defects at the surface terrace of $\text{ZnO}(10\bar{1}0)$, exhibiting an apparent depth of ~ 50 pm for type I depression and ~ 110 pm for type II depression (Fig. 1(e)), respectively. Recently, we reported on the presence of Zn-O dimer vacancies as a characteristic defect structure on $\text{ZnO}(10\bar{1}0)$, based on STM observation and DFT simulation [29]. The depth profile of type II depressions suggested that they could be assigned as Zn-O dimer vacancies on $\text{ZnO}(10\bar{1}0)$. Meanwhile, the adsorption of CO on $\text{ZnO}(10\bar{1}0)$, where CO is bonded to surface Zn site, would also introduce dark spot in the Zn row in STM images [30]. Fig. 1(d) showed a STM image of the $\text{ZnO}(10\bar{1}0)$ surface after CO exposure. The depth profile of the depression induced by CO adsorption is similar to that observed for type I depression, which could thus be assigned as CO adsorption on Zn rows, caused by background CO during

Fig. 1. STM images of clean and CO adsorbed surface of ZnO(10 $\bar{1}$ 0). (a) Large-scale image of clean ZnO(10 $\bar{1}$ 0). Inset is the atomically resolved STM image. The squared area in (a) is magnified in (b). Current-mode STM image of (b) is shown in (c) to enhance the contrast of depressions. (d) Surface adsorbed with CO molecules. Line profiles in (b) and (d) are plotted in (e) to differentiate the apparent heights of surface defects and CO-adsorption-induced depressions. (f) Ball-stick model for CO adsorption and Zn-O vacancy ($V_{\text{Zn-O}}$). Scanning conditions: (a) $V_s=1.5$ V, $I_t=0.1$ nA; inset, $V_s=0.66$ V, $I_t=0.5$ nA; (b) $V_s=0.8$ V, $I_t=0.5$ nA; (d) $V_s=2.0$ V, $I_t=0.05$ nA.

imaging at LT. Therefore, type I and II depressions observed on ZnO(10 $\bar{1}$ 0) could be attributed to CO adsorption on surface Zn site and Zn-O dimer vacancy, respectively. Their structural models are illustrated in Fig. 1(f).

3.2. Growth and Structures of Cr on ZnO(10 $\bar{1}$ 0)

The growth of Cr on ZnO(10 $\bar{1}$ 0) was subsequently studied

under various deposition and annealing temperatures. Fig. 2 showed STM images of Cr atoms deposited on ZnO(10 $\bar{1}$ 0) surfaces at 300 K. At ~ 0.075 ML (Fig. 2(a)–(d)), as-deposited Cr atoms appeared mostly as isolated atomic features on or in the surface lattice of ZnO(10 $\bar{1}$ 0), while rectangular islands caused by Cr deposition could also be observed, nucleating at step edges along the [0001] direction. The atomic features of as-deposited Cr atoms are categorized into two types, Cr_A and

Fig. 2. Surface structures of Cr deposited on ZnO(10 $\bar{1}$ 0) at 300 K. (a–c) STM images of 0.075 ML Cr deposited on ZnO(10 $\bar{1}$ 0). The white squared area in (a) is magnified in the inset. Cr atoms adsorbed on or embedded in the surface of ZnO(10 $\bar{1}$ 0) are demonstrated in (b,c) and termed as Cr_A and Cr_B , respectively. Cr_A atoms were imaged as bright protrusions at below +1.5 V sample bias. Line profiles in (a) and (b) are plotted in (d). (e,f) High-resolution STM images of Cr atoms on ZnO(10 $\bar{1}$ 0). CO adsorption on Zn sites was used to confirm the location of Zn rows. The red and blue arrows indicate the positions of Cr_A adatom on surface and Cr_B atoms in Zn rows, respectively. Cr_B atoms were resolved as bright dots with dark halos due to the change of tip state. (f) Side and top views of the structural model of Cr atoms on ZnO(10 $\bar{1}$ 0). Gray, red and pink balls represent Zn, O and Cr atoms, respectively. Red and blue cycles indicate the locations of Cr_A on the O row, and Cr_B substituting Zn atom in the Zn row, respectively. Scanning conditions: (b) $V_s=1.0$ V, $I_t=0.5$ nA; (c) $V_s=1.5$ V, $I_t=0.2$ nA; (e) $V_s=1.2$ V, $I_t=0.3$ nA.

Fig. 3. STM images of 0.2 ML Cr/ZnO(10 $\bar{1}$ 0) (a–c) and 0.4 ML Cr/ZnO(10 $\bar{1}$ 0) (d–f) prepared by depositing Cr atoms onto ZnO(10 $\bar{1}$ 0) at 300 K. Squared region in (a) is magnified in (c). With increasing Cr coverage, both the density of surface Cr atoms and the size of Cr islands increased. To enhance the contrast, current-mode STM images were displayed in (b) and (e).

Cr_B, based on their apparent heights in STM. Cr_A atoms are imaged as bright protrusions surrounded by a dark halo and found located uniformly between on the Zn rows on ZnO(10 $\bar{1}$ 0) (Fig. 2(c)). On the other hand, Cr_B atoms are dark depressions located in the Zn rows. From the line profile, Cr_B exhibited an apparent depth at $\sim$ 0.2 nm (Fig. 2(d)), which is larger than those of surface defects or CO adsorption on ZnO(10 $\bar{1}$ 0).

Statistical analysis on the surface atomic features (> 200 Cr atoms in STM images) showed that > 60% Cr atoms are Cr_A atoms at $\sim$ 0.075 ML Cr surface coverage when Cr was deposited at 300 K. Using CO molecules bonding to Zn sites as the markers, the atomic structures of Cr atoms on or in the surface lattice of ZnO(10 $\bar{1}$ 0) could be identified (Fig. 2(e)) and their structural models were displayed in Fig. 2(f). Cr_A atom between the Zn rows was found to attached to the O row and sat between two oxygen atoms in the O row rather than on top of the O atom. Meanwhile, Cr_B atoms were found substituting Zn atoms in the Zn rows and their depressions were an electronic effect, caused by their charge transfer to neighboring Zn sites. Note that, upon tip change, Cr_B atoms in the Zn rows could also be resolved with an increased apparent height, where dark circle around Cr_B could be visualized (Fig. 2(e)).

As surface Cr coverage increases, Fig. 3 showed that the density of Cr_A atoms increases accompanying the density in-

crease of rectangular islands. Compared to the 0.075 ML Cr/ZnO(10 $\bar{1}$ 0) surface, the size of rectangular islands on 0.2 ML Cr/ZnO(10 $\bar{1}$ 0) did not exhibit an obvious increase, while their average height increased slightly from $\sim$ 1.1 to $\sim$ 1.3 nm, implying the growth of one Cr layer (Figs. 3(a) and (b)) if Cr adopts the BCC-Cr(110) structure [31]. Yet, the interfacial layer between Cr islands and ZnO might adopt a different structure, as reflected by the odd value of the apparent height of Cr islands. To enhance the contrast, current-mode STM image was used to display the large-scale morphology (Fig. 3(b)). We have thus assigned these rectangular islands as Cr islands, which grew preferentially along the [0001] direction. The growth of Cr atoms also caused the appearance of bright features on the ZnO(10 $\bar{1}$ 0) surface (Fig. 3(c)), which could be attributed to the electronic perturbation caused by Cr deposition or the distortion of ZnO surface lattice induced by the incorporation of Cr into the ZnO surface lattice. For the 0.4 ML Cr/ZnO(10 $\bar{1}$ 0) surface (Figs. 3(d)–(f)), both the increased density of Cr adatoms and the continuous growth of Cr islands could be observed, where the average dimensions of Cr islands were $\sim$ 5.3 nm in width, 7.6 nm in length and 1.7 nm in height. Surface morphology of ZnO(10 $\bar{1}$ 0) became more corrugated, although no growth of three-dimensional (3D) Cr clusters were obvious from their apparent height.

The growth behavior of Cr on ZnO(10 $\bar{1}$ 0) appeared drastically different from other transition metals on ZnO reported previously, or even the typical growth modes of metal nanoparticles (NPs) on oxides. In comparison, the surface morphology of 0.06 ML Cu deposited on ZnO(10 $\bar{1}$ 0) at 300 K was displayed in Fig. 4, which showed a 3D growth of supported Cu clusters. Previous studies have also suggested that Cu on ZnO(10 $\bar{1}$ 0) exhibited exclusively a 3D growth at even 0.025 ML surface coverage [32,33], where a preferential nucleation at step edges along the [0001] direction could be observed. Meanwhile, 0.05 ML Au grew on ZnO(10 $\bar{1}$ 0) in the form of 2D islands and dispersed evenly across the surface [33]. As Co atoms were deposited on ZnO(10 $\bar{1}$ 0) at 300 K, a uniform (2 $\times$ 1) superstructure was observed at 0.5 ML Co surface coverage [34]. Owing to the strong interaction between Cr and ZnO, the diffusion of Cr is limited, resulting in the atomic dispersion of Cr atoms on ZnO(10 $\bar{1}$ 0). However, the formation of rectangular Cr islands at step edges remained to be explained. Patterson et al. [33] reported that Cu adatoms on ZnO(10 $\bar{1}$ 0) showed significantly anisotropic diffusion barriers of 0.29 eV along [1 $\bar{2}$ 10]

Fig. 4. STM images of 0.06 ML Cu/ZnO(10 $\bar{1}$ 0) prepared by depositing Cu onto ZnO(10 $\bar{1}$ 0) at 300 K. (a,b) STM images showing the 3D growth of Cu clusters, which nucleated both at step edges and on the surface terrace. Line profile in (b) is plotted in (c) to exemplify the 3D growth of Cu clusters.

and 1.04 eV along [0001], resulting in clustering at step edge along [0001]. Similarly, anisotropic diffusion of Cr could explain the rectangular shape of Cr islands. The preferential nucleation of Cr islands at step edges indicated a particular strong interaction between the [0001] steps of ZnO(10 $\bar{1}$ 0) and Cr, where the growth mechanism requires further studies.

We compared further the growth of Cr on ZnO(10 $\bar{1}$ 0) at varying temperatures (Fig. 5). When Cr was deposited onto ZnO(10 $\bar{1}$ 0) at 200 K, the formation of round Cr clusters was observed on ZnO (Figs. 5(a) and (b)). The disappearance of large rectangular Cr islands could be attributed to the limited diffusion of Cr atoms at low temperature, which inhibited the formation of Cr nucleus at step edges and caused the random distribution of Cr clusters across the surface terrace. At 200 K, almost all atomic Cr features were Cr_A atoms, indicating the substitution of Zn sites by Cr atoms was kinetically inhibited at 200 K. In comparison, when Cr was deposited onto ZnO(10 $\bar{1}$ 0) at 400 K, Cr atoms were found dispersed into the ZnO lattice. Neither Cr islands or Cr_A atoms were obvious on the ZnO(10 $\bar{1}$ 0) surface (Figs. 5(c) and (d)), owing to the strong interaction between Cr and ZnO. A few bright dots on the Zn rows could be observed, which could be assigned as impurities or Zn atoms out of the surface plane due to the lattice distortion caused by Cr incorporation.

We also studied the annealing effect on the surface morphology of Cr on ZnO(10 $\bar{1}$ 0). Figs. 5(e) and (f) showed a typical surface 0.15 ML Cr/ZnO(10 $\bar{1}$ 0), where Cr was deposited at 300 K. Upon the annealing at 600 K in UHV, both Cr islands and Cr_A atoms were found to disappear from the surface (Figs. 5(g) and (h)). Instead, all surface Cr atoms were found as atomic dark depressions, i.e. Cr atoms replacing Zn sites in the ZnO lattice. Thus, Cr islands on ZnO are not stable and could be re-dispersed atomically into the ZnO lattice upon thermal annealing. In comparison, the annealing in UHV would usually cause the coarsening of 3D Cu clusters on ZnO at 300–465 K, and enhance the formation of a wetting Cu layer at 465–560 K, owing to the migration of subsurface oxygen vacancies towards the surface [35]. The facile incorporation of Cr into the ZnO

lattice could be attributed to the formation of a precursor phase for the transformation into the ZnCr₂O₄ spinel structure, which is thermodynamically preferred. We have tried to induce the formation of ZnCrO_x surface phase by the oxidation of the Cr/ZnO(10 $\bar{1}$ 0) surface in O₂ at elevated temperatures. However, the oxidation is accompanied by the loss of surface conductivity and brought difficulties for further structural characterization.

3.3. Electronic structures of Cr on ZnO(10 $\bar{1}$ 0)

The chemical states of Cr on ZnO(10 $\bar{1}$ 0) were studied by XPS. Often time, Cr 2p was used to determine the oxidation states of Cr. We found that, when using the Al K α source, Zn LMM Auger lines would interfere with the Cr 2p spectra (Fig. 6(a)) and could cause misinterpretation of chemical states of Cr in the Cr-ZnO system. To identify the chemical states of Cr, we tried to use the differential spectra, i.e. to subtract XPS Cr 2p spectra of the Cr/ZnO(10 $\bar{1}$ 0) sample with that of clean ZnO(10 $\bar{1}$ 0). However, the overlapping between Zn LMM Auger and Cr 2p at binding energies (BEs) between 576 and 586 eV caused very weak signal and poor signal-to-noise ratio for low coverage Cr on ZnO(10 $\bar{1}$ 0), as manifested by the differential spectra of Cr 2p for 0.2 ML Cr/ZnO(10 $\bar{1}$ 0) (Fig. 6(c)). Apparently, it is difficult to distinguish the oxidation states of Cr from Fig. 6(c). For 0.8 ML Cr/ZnO(10 $\bar{1}$ 0), the differential Cr 2p spectra (Fig. 6(b)) showed that the BE of Cr 2p_{3/2} was located at 574.8 eV upon Cr deposition, indicating the presence of metallic state for 0.8 ML Cr [36,37]. The exposure to 1 $\times$ 10⁻⁶ mbar CO at 300 K led to no obvious adsorption signal of CO in C 1s spectra at 300 K (not shown) and no change in the Cr 2p spectra was detected. When the sample was annealed at above 450 K, the BE of Cr 2p_{3/2} shifted to 576.7 eV, suggesting the oxidation of Cr into Cr³⁺, consistent with STM results on the decomposition of Cr islands and the incorporation of Cr into the ZnO lattice.

As an alternative, we also used XPS Cr 3p spectra to examine the chemical states of Cr on ZnO(10 $\bar{1}$ 0) [38,39]. Figs. 6(d) and (e) showed Cr 3p spectra of the 0.06 ML Cr/ZnO(10 $\bar{1}$ 0) and 0.2 ML Cr/ZnO(10 $\bar{1}$ 0) surfaces, acquired with the excitation pho-

Fig. 5. STM images of the temperature effect on the surface structures of Cr/ZnO(10 $\bar{1}$ 0). (a,b) Cr atoms (0.075 ML) deposited at ~200 K. Cr clusters and surface Cr atoms were both observed. (c,d) Cr atoms (0.075 ML) deposited at 400 K. The incorporation of Cr atoms into the ZnO lattice is clearly observed in (d). (e,f) A typical surface of 0.15 ML Cr/ZnO(10 $\bar{1}$ 0), where Cr was deposited at 300 K. (g,h) The surface in (e) was annealed at 600 K under UHV. Cr islands would decompose and incorporate into the ZnO lattice after annealing. Scanning conditions: (b) $V_s=1.0$ V, $I_t=0.2$ nA; (d) $V_s=1.2$ V, $I_t=0.1$ nA; (f) $V_s=1.0$ V, $I_t=0.5$ nA; (h) $V_s=0.8$ V, $I_t=0.2$ nA.

Fig. 6. XPS spectra on the oxidation states of Cr on ZnO(10 $\bar{1}$ 0). (a–c) Cr 2p spectra collected with Al K α source. (a) Cr 2p spectra on the clean ZnO(10 $\bar{1}$ 0) and 0.8 ML Cr/ZnO(10 $\bar{1}$ 0). Cr 2p spectra of the latter surface annealed in 1×10^{-6} mbar CO at different temperatures were displayed sequentially. (b) The differential spectra of 0.8 ML Cr/ZnO(10 $\bar{1}$ 0) obtained by subtracting Cr 2p spectra in (a) by the Cr 2p spectrum of clean ZnO(10 $\bar{1}$ 0) (black curve). (c) The differential Cr 2p spectra of 0.2 ML Cr/ZnO(10 $\bar{1}$ 0). (d,e) Cr 3p spectra of (d) 0.06 ML Cr/ZnO(10 $\bar{1}$ 0) and (e) 0.2 ML Cr/ZnO(10 $\bar{1}$ 0) before and after the annealing in 1×10^{-6} mbar CO at different temperatures.

ton energy of 120 eV. On 0.06 ML Cr/ZnO(10 $\bar{1}$ 0), Cr 3p spectra gave a peak at 44.0 eV [39], which could be attributed to Cr³⁺ and suggest that Cr atoms on ZnO(10 $\bar{1}$ 0), as observed in STM were positively charged. On 0.2 ML Cr/ZnO(10 $\bar{1}$ 0), a new peak at 42.1 eV in the Cr 3p spectra suggested the presence of metallic Cr, in accordance with STM measurements (Fig. 3). After the annealing at 450 K in UHV, Cr 3p spectra indicated that metallic Cr atoms were transformed into Cr³⁺, which could be attributed to the incorporation of Cr atoms into the surface lattice of ZnO. Consistent with STM observations, XPS results confirmed that at low Cr coverage (< 0.1 ML), as-deposited Cr atoms are present mainly in the form of Cr³⁺, while with increasing Cr coverage, metallic Cr became dominant, which would transform into Cr³⁺ after the annealing at above 450 K. The intensity of Cr 3p peaks attenuated obviously after the annealing at 670 K, indicating the diffusion of Cr atoms into subsurface or even the bulk, although there are still Cr atoms in the surface lattice.

3.4. CO adsorption on Cr/ZnO(10 $\bar{1}$ 0)

We then used CO as a probe molecule to examine the adsorption properties of the Cr/ZnO(10 $\bar{1}$ 0) surface. Previous studies have shown CO adsorbs weakly on ZnO and its adsorption energy on Zn site of ZnO(10 $\bar{1}$ 0) is only $-0.24 \sim -0.38$ eV [30,40]. On Cr-terminated Cr₂O₃(0001), the adsorption energy

of CO was determined to be ~ -0.47 eV [41]. We studied the adsorption of CO on Cr/ZnO(10 $\bar{1}$ 0) at 78 K. Figs. 7(a)–(d) suggested that there were no preferential adsorption of CO on either Cr_A atoms or Cr_B atoms at 78 K. Whether Cr atoms were on surface (Figs. 7(a) and (b)) or in the ZnO lattice (Figs. 7(c) and (d)), the exposure of CO resulted in random adsorption on the surface terrace. We also studied the adsorption of CO on Cr/ZnO(10 $\bar{1}$ 0) at elevated temperatures. Owing to the weak adsorption of CO on Cr/ZnO(10 $\bar{1}$ 0), which desorbs at below 300 K, no significant morphological change was observed even when the Cr/ZnO(10 $\bar{1}$ 0) surface was annealed in CO (Figs. 7(e) and (f)) compared with annealing under UHV conditions (Figs. 5(g) and (h)). Density functional theory (DFT) study also suggested that doping Cr into the bulk or surface of ZnO(10 $\bar{1}$ 0) would not facilitate the formation of oxygen vacancies unless the ZnCr₂O₄ spinel structure was formed [7].

Fig. 8 displayed O 1s and Zn 2p_{3/2} spectra on the interaction between CO and 0.2 ML Cr/ZnO(10 $\bar{1}$ 0) under high vacuum. O 1s spectra exhibited a sharp peak at 530.8 eV for lattice oxygen of ZnO and an additional shoulder peak at ~ 532.8 eV upon CO exposure at 300 K, which was assigned to oxygen from surface carbonate species (Fig. 8(a)) [42]. The shoulder peak disappeared after the annealing at 450 K. Zn 2p_{3/2} peaks at 1021.7 eV showed almost the same symmetrical shapes as clean ZnO except for slight attenuation of peak intensity (Fig. 8(b)). Inter-

Fig. 7. STM images on the effects of Cr doping on CO adsorption on ZnO(10 $\bar{1}$ 0). (a,b) CO adsorption at 78 K on 0.075 ML Cr/ZnO(10 $\bar{1}$ 0) surface prepared by depositing Cr onto ZnO(10 $\bar{1}$ 0) at 300 K. The squared region in (a) is magnified in (b). (c,d) In situ STM images before (c) and after (d) the adsorption of CO at 78 K on the 0.075 ML Cr/ZnO(10 $\bar{1}$ 0) surface, which was prepared by Cr deposition at 400 K. (e,f) STM images of 0.075 ML Cr/ZnO after the annealing in 1×10^{-6} mbar CO at 600 K.

estingly, after the annealing at 670 K in 1×10^{-6} mbar CO, O 1s peak showed large negative shift of ~ 0.6 eV for the 0.2 ML Cr/ZnO(10 $\bar{1}$ 0) surface, while the Zn 2p $_{3/2}$ peak showed the same negative shift of binding energy by ~ 0.6 eV after annealing. To exclude the influence of charging effects related with poor conductivity of ZnO, five Cr/ZnO(10 $\bar{1}$ 0) samples with surface Cr coverages ranging from 0.06 ML to 2.0 ML were examined with XPS. Consistently, the shift to lower binding energy

was found to be ~ 0.5 eV for low Cr coverage (< 0.12 ML), and 0.6–0.7 eV for Cr coverage between 0.2–2.0 ML. The energy shifts for O 1s and Zn 2p $_{3/2}$ peaks were plotted as a function of surface Cr coverage in Fig. 8(c). Note that, the Cr 2p peaks also shifted after the annealing at 670 K and the differential spectra of Cr 2p in Figs. 6(b) and (c) were derived considering the negative shift of Cr peaks by 0.6–0.65 eV. We attributed the shift of core level peaks after annealing to the upward band bending effect often observed in the metal-oxide heterojunction [34,35,43,44]. In brief, after the dispersion of Cr atoms into bulk ZnO lattice, charge redistribution between Cr and ZnO in the near-surface region could lead to an internal electronic field perpendicular to the crystal surface in the near-surface region.

4. Conclusions

Using LT-STM and XPS, we investigated the growth, structure and electronic properties of Cr on ZnO(10 $\bar{1}$ 0). Our results suggested that when deposited at 300 K, at low surface coverage (< 0.1 ML), Cr grew dominantly as isolated atoms on the surface terrace of ZnO or substituting Zn sites in the ZnO lattice, resulting in the formation of Cr $^{3+}$ on ZnO. The nucleation of rectangular islands, assigned as Cr islands, at the step edges along the [0001] direction could also be observed even during the initial growth of Cr. Such growth behavior is drastically different from the growth of other late transition metals, such as Cu and Au on ZnO, where they typically exhibit 3D or 2D cluster growth at 300 K. At increasing Cr coverages, the surface is characterized with increasing density of Cr atoms, which would disperse into the ZnO lattice after the annealing at above 600 K. The annealing would also cause the disappearance of Cr islands, which decompose and re-disperse into the ZnO bulk. The substrate temperature for Cr growth has a significant effect on the morphology of Cr on ZnO(10 $\bar{1}$ 0), where deposited Cr was found dominantly as Cr $^{3+}$ ions in the ZnO lattice. Our study thus demonstrated the strong interaction between Cr and ZnO, although no preferred adsorption of CO on the lattice Cr sites was observed at 78 K. When the Cr-doped ZnO surface was annealed at above 600 K, a negative shift of core level peaks was observed for Zn and O, indicating an upward band bending

Fig. 8. O 1s and Zn 2p $_{3/2}$ spectra of 0.2 ML Cr/ZnO(10 $\bar{1}$ 0) before and after the annealing at different temperatures in 1×10^{-6} mbar CO. (a) O 1s spectra taken with incident X-ray photon energy at 600 eV. After annealing in 1×10^{-6} mbar CO at 670 K, a negative shift by ~ 0.6 eV was observed. (b) Zn 2p $_{3/2}$ spectra taken with Al K α source. (c) Shift of core-level binding energies of O 1s and Zn 2p $_{3/2}$ as a function of Cr coverage.

effect due to the charge redistribution when Cr atoms were dissolved into the ZnO lattice. Our study has thus provided an effective way to synthesize Cr/ZnO model system, which is suitable for further model catalytic studies.

References

- [1] S. Kattel, P. J. Ramírez, J. G. Chen, J. A. Rodriguez, P. Liu, *Science*, **2017**, 355, 1296–1299.
- [2] S. Kuld, M. Thorhauge, H. Falsig, C. F. Elkjær, S. Helveg, I. Chorkendorff, J. Sehested, *Science*, **2016**, 352, 969–974.
- [3] F. Jiao, J. Li, X. Pan, J. Xiao, H. Li, H. Ma, M. Wei, Y. Pan, Z. Zhou, M. Li, S. Miao, J. Li, Y. Zhu, D. Xiao, T. He, J. Yang, F. Qi, Q. Fu, X. Bao, *Science*, **2016**, 351, 1065–1068.
- [4] N. Li, F. Jiao, X. Pan, Y. Ding, J. Feng, X. Bao, *ACS Catal.*, **2019**, 9, 960–966.
- [5] J. A. Rodriguez, P. Liu, J. Hrbek, J. Evans, M. Perez, *Angew. Chem. Int. Ed.*, **2007**, 46, 1329–1332.
- [6] S. Ma, S.-D. Huang, Z.-P. Liu, *Nat. Catal.*, **2019**, 2, 671–677.
- [7] H. Song, D. Laudenschleger, J. J. Carey, H. Ruland, M. Nolan, M. Muhler, *ACS Catal.*, **2017**, 7, 7610–7622.
- [8] K. Cheng, B. Gu, X. Liu, J. Kang, Q. Zhang, Y. Wang, *Angew. Chem. Int. Ed.*, **2016**, 55, 4725–4728.
- [9] J. Wang, G. Li, Z. Li, C. Tang, Z. Feng, H. An, H. Liu, T. Liu, C. Li, *Sci. Adv.*, **2017**, 3, e1701290.
- [10] X. Liu, M. Wang, C. Zhou, W. Zhou, K. Cheng, J. Kang, Q. Zhang, W. Deng, Y. Wang, *Chem. Commun.*, **2018**, 54, 140–143.
- [11] T. Minato, *Chem Rec*, **2014**, 14, 923–934.
- [12] Z. Dohnálek, I. Lyubnitsky, R. Rousseau, *Prog. Surf. Sci.*, **2010**, 85, 161–205.
- [13] W.-J. Yin, B. Wen, C. Zhou, A. Selloni, L.-M. Liu, *Surf. Sci. Rep.*, **2018**, 73, 58–82.
- [14] O. Dulub, L. A. Boatner, U. Diebold, *Surf. Sci.*, **2002**, 519, 201–217.
- [15] Y. Wang, R. Kovacic, B. Meyer, K. Kotsis, D. Stodt, V. Staemmler, H. Qiu, F. Traeger, D. Langenberg, M. Muhler, C. Woll, *Angew. Chem. Int. Ed.*, **2007**, 46, 5624–5627.
- [16] F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, R. Rosei, *Science*, **2005**, 309, 752–755.
- [17] S. Torbrügge, M. Reichling, A. Ishiyama, S. Morita, Ó. Custance, *Phys. Rev. Lett.*, **2007**, 99, 056101.
- [18] J. A. Rodriguez, D. C. Grinter, Z. Liu, R. M. Palomino, S. D. Senanayake, *Chem. Soc. Rev.*, **2017**, 46, 1824–1841.
- [19] U. Diebold, S. C. Li, M. Schmid, *Annu. Rev. Phys. Chem.*, **2010**, 61, 129–148.
- [20] C. Woll, *Prog. Surf. Sci.*, **2007**, 82, 55–120.
- [21] L. Li, W. Wang, H. Liu, X. Liu, Q. Song, S. Ren, *J. Phys. Chem. C*, **2009**, 113, 8460–8464.
- [22] F. Stavale, X. Shao, N. Nilus, H. J. Freund, S. Prada, L. Giordano, G. Pacchioni, *J. Am. Chem. Soc.*, **2012**, 134, 11380–11383.
- [23] J. H. Park, M. G. Kim, H. M. Jang, S. Ryu, Y. M. Kim, *Appl. Phys. Lett.*, **2004**, 84, 1338–1340.
- [24] R. Bechstein, M. Kitta, J. Schütte, A. Kühnle, H. Onishi, *J. Phys. Chem. C*, **2009**, 113, 3277–3280.
- [25] Y. Wang, B. Meyer, X. Yin, M. Kunat, D. Langenberg, F. Traeger, A. Birkner, C. Woll, *Phys. Rev. Lett.*, **2005**, 95, 266104.
- [26] C. G. Van de Walle, *Phys. Rev. Lett.*, **2000**, 85, 1012–1015.
- [27] U. Diebold, L. V. Koplitz, O. Dulub, *Appl. Surf. Sci.*, **2004**, 237, 336–342.
- [28] R. Kovacic, B. Meyer, D. Marx, *Angew. Chem. Int. Ed.*, **2007**, 46, 4894–4897.
- [29] Y. Cao, J. Luo, W. Huang, Y. Ling, J. Zhu, W. X. Li, F. Yang, X. Bao, *J. Chem. Phys.*, **2020**, 152, 074714.
- [30] H. Shi, H. Yuan, S. Ruan, W. Wang, Z. Li, Z. Li, X. Shao, *J. Phys. Chem. C*, **2018**, 122, 8919–8924.
- [31] V. Maurice, W. P. Yang, P. Marcus, *J. Electrochem. Soc.*, **1994**, 141, 3016–3027.
- [32] O. Dulub, L. A. Boatner, U. Diebold, *Surf. Sci.*, **2002**, 504, 271–281.
- [33] M. C. Patterson, X. Nie, F. Wang, R. L. Kurtz, S. B. Sinnott, A. Asthagiri, P. T. Sprunger, *J. Phys. Chem. C*, **2013**, 117, 18386–18397.
- [34] S. H. Su, J. H. Lai, H.-H. Chen, T.-H. Lee, Y.-J. Hsu, R. L. Wang, J. C. A. Huang, *J. Phys. Chem. C*, **2012**, 116, 9917–9924.
- [35] I. Beinik, M. Hellstrom, T. N. Jensen, P. Broqvist, J. V. Lauritsen, *Nat. Commun.*, **2015**, 6, 8845.
- [36] D. Guo, Q. Guo, M. S. Altman, E. G. Wang, *J. Phys. Chem. B*, **2005**, 109, 20968–20972.

Graphical Abstract

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Atomic structures and electronic properties of Cr-doped ZnO(10 $\bar{1}$ 0) surfaces

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Cr islands and isolated Cr³⁺ atoms deposited on ZnO(10 $\bar{1}$ 0) at 300 K would re-disperse into ZnO lattice after annealing at above 600 K owing to the strong interaction between Cr and ZnO.

- [37] M. Hassel, I. Hemmerich, H. Kühlenbeck, H. J. Freund, *Surf. Sci. Spectra*, **1996**, 4, 246–252.
- [38] M. Detroye, F. Reniers, C. Buess-Herman, J. Vereecken, *Appl. Surf. Sci.*, **1999**, 144–145, 78–82.
- [39] C. Battistoni, J. L. Dormann, D. Fiorani, E. Paparazzo, S. Viticoli, *Solid State Commun.*, **1981**, 39, 581–585.
- [40] B. Meyer, D. Marx, *J. Phys. Condens. Matter*, **2003**, 15, L89–L94.
- [41] M. Pykavy, V. Staemmler, O. Seiferth, H. J. Freund, *Surf. Sci.*, **2001**, 479, 11–25.
- [42] T. Becker, M. Kunat, C. Boas, U. Burghaus, C. Wöll, *J. Chem. Phys.*, **2000**, 113, 6334–6343.
- [43] P. Blumentrit, M. Yoshitake, S. Nemšák, T. Kim, T. Nagata, *Appl. Surf. Sci.*, **2011**, 258, 780–785.
- [44] K. Ozawa, K. Edamoto, *Surf. Sci.*, **2003**, 524, 78–88.

Cr掺杂ZnO(10 $\bar{1}$ 0)表面的原子结构和电子性质研究

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摘要: 多相催化中ZnO基催化剂广泛应用于甲醇合成、水汽变换和合成气转化等诸多领域。近期发展的ZnCrO_x-分子筛双功能催化剂(OX-ZEO)打破了传统合成气转化的ASF分布, 能够高选择性地实现CO加氢转化为低碳烯烃。其中CO在ZnCrO_x表面活化被认为是OX-ZEO催化的关键基元过程, 但是ZnCrO_x表面的活性位组成和结构目前仍然缺乏原子尺度上的理解, 阻碍了人们对反应机理的研究。因此, 本文构建了Cr掺杂ZnO(10 $\bar{1}$ 0)单晶的模型催化剂, 结合低温扫描隧道显微镜(LT-STM)和X射线光电子能谱(XPS), 研究不同条件下Cr在ZnO(10 $\bar{1}$ 0)表面生长的形貌结构, 并重点考察了Cr掺杂对表面电子结构和CO吸附的影响。

ZnO(10 $\bar{1}$ 0)是Zn-O混合终止的非极性面, 也是ZnO最稳定的晶面。实验发现室温下沉积Cr在ZnO(10 $\bar{1}$ 0)表面时, 出现多种生长结构。STM显示低覆盖率(< 0.1 ML)的沉积Cr在ZnO(10 $\bar{1}$ 0)台阶面上出现单分散的亮点和暗点, 分别为位于表面O原子链上的Cr原子和嵌入ZnO晶格替代Zn²⁺的Cr。XPS显示这些Cr原子与ZnO之间存在电荷转移, 呈现出+3价。由于Cr在[0001]方向扩散能垒高于沿着[1 $\bar{2}$ 10]方向扩散的能垒, 能够观察到少量沿着[0001]台阶方向生长的长方形岛, 归属为Cr岛。表面单分散Cr原子和Cr岛的密度都会随着Cr沉积量的增加而增多。当在200 K沉积Cr来抑制Cr的表面扩散行为, 我们发现Cr主要在ZnO面上形成Cr团簇, 均匀分散在表面; 而在400 K沉积时, Cr则直接扩散进入ZnO晶格。STM和XPS结果都表明, 600 K以上的高温处理能够促进Cr进入ZnO晶格, 同时伴随Cr岛的分解, 这说明表面负载的Cr原子在高温不能稳定存在; 而Cr岛的再分散进入到近表层甚至体相, 也表明了Cr和ZnO之间的强相互作用。这种强相互作用有利于Cr在ZnO表层进行原子级分散, 形成具有催化活性的结构; 与此同时, 实验发现Cr扩散到近表层会导致表面能带向上弯曲, 从而导致XPS芯能级向低结合能位移。在超高真空条件下, CO与Cr掺杂的ZnO表面作用较弱, 室温下只观察到碳酸盐的形成。

因此, 通过对比不同条件下Cr在ZnO(10 $\bar{1}$ 0)表面的生长结构, 热稳定性以及相应的电子结构变化, 发现Cr和ZnO存在强相互作用, 在600 K以上Cr以Cr³⁺形式分散到ZnO晶格中。本文通过构建Cr/ZnO(10 $\bar{1}$ 0)模型催化剂, 并研究其原子结构与电子结构的演变, 为进一步的分子尺度合成气转化机理研究开辟了道路。

关键词: ZnO; Cr/ZnO(10 $\bar{1}$ 0)催化剂; CO吸附; STM; XPS

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