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Article (Special Issue in Memory of the 80th Birthday of Professor Jingfa Deng)

XPS and TPD study of NO interaction with Cu(111): Role of different oxygen species

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ARTICLE INFO

Article history:

Received 5 January 2013

Accepted 4 February 2013

Published 20 May 2013

Keywords:

Nitrogen oxide

Cu(111)

Oxygen species

Adsorption

Temperature-programmed desorption

X-ray photoelectron spectroscopy

ABSTRACT

The adsorption and reaction of NO on clean and O-precovered Cu(111) has been studied using X-ray photoelectron spectroscopy and temperature-programmed desorption spectroscopy. By varying NO exposure and annealing temperature, two different types of chemisorbed oxygen species, with O 1s binding energies (BE) of 531.0 (O₅₃₁) and 529.7 eV (O₅₂₉), were prepared on Cu(111). In the presence of O₅₃₁ species, the relative occupation of different NO adsorption states was largely affected, and most of the adsorbed NO(a) underwent dissociative desorption, releasing N₂O and N₂ upon heating. In contrast, in the presence of O₅₂₉ species, the dissociative desorption of NO(a) was largely suppressed. Furthermore, the O₅₂₉ species show a more significant blocking effect on NO adsorption than the chemisorbed O₅₃₁ species. Our results reveal that the effect of precovered oxygen species on the adsorption and reaction of NO on Cu(111) is closely related to the type of oxygen species and oxygen coverage.

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1. Introduction

Cu-based catalysts have attracted much attention over the past few decades because they can be widely applied in many catalytic reactions including CO oxidation, water-gas shift, NO decomposition, CO hydrogenation, etc. [1–6]. The excellent catalytic performance of Cu-based catalysts, particularly in the oxidation reaction, has been attributed to the Cu oxidation state and specific active oxygen species involved in the facile redox chemistry of these catalysts. For example, in-situ photoelectron spectroscopy measurements of methanol oxidation on Cu(111) have demonstrated that sub-surface oxygen plays an important

role in the formation of formaldehyde, while the oxide phase promotes combustion into CO₂ [7]. Therefore, studying the effect of various oxygen species on the chemical properties of Cu surfaces is necessary for deep understanding of related reaction mechanisms at the atomic level. In the present study, different types of oxygen species were produced by controlled decomposition of NO on Cu(111) and these substrates were compared to those prepared by the normal method of molecular oxygen exposure.

The interaction of NO on Cu surfaces has been extensively investigated [8–26]. However, there is still some disagreement on the adsorption behavior of NO on Cu(111). On the basis of

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This work was supported by the National Natural Science Foundation of China (21073172), the National Basic Research Program of China (973 Program, 2013CB933104, 2013CB933102, 2010CB923301), and the Fundamental Research Funds for the Central Universities.

DOI: 10.1016/S1872-2067(12)60585-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 5, May 2013

high resolution electron energy loss spectroscopy (HREELS) measurements, it has been suggested that NO initially occupies bridge sites on Cu(111) at low coverage, and that the bridge-bonded NO is replaced by linearly-adsorbed NO at higher NO coverage [10,13]. Sueyoshi et al. [19] proposed a mixture structure containing NO adsorbed on both atop and 3-fold hollow sites. However, Dumas et al. [21], using infrared reflection absorption spectroscopy (IRAS), concluded that NO adsorbs exclusively on 3-fold hollow sites of Cu(111) up to one monolayer at 90 K. Even at temperatures as low as 85 K, the formation of $\text{N}_2\text{O}(\text{a})$ and $\text{O}(\text{a})$ occurs through an $(\text{NO})_2$ intermediate, the presence of which was identified by IRAS at higher NO exposure [21]. Desorption of $\text{N}_2\text{O}(\text{a})$ was observed to start at around 110–120 K leaving $\text{O}(\text{a})$ on the surface [10,13,21,27]. Other Cu surfaces such as Cu(100) and Cu(110) exhibit similar adsorption behavior, but display even greater NO reactivity [17,25]. In spite of the above previous studies, which mostly focus on the adsorption and desorption behavior of NO, less attention has been paid to the state of the oxygen species resulting from Cu-NO interaction.

In the present study, the adsorption and interaction of NO on clean and O-precovered Cu(111) surfaces have been studied by X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) measurements. By varying NO exposure and annealing temperature, different oxygen species were prepared on the surface. Furthermore, the effect of various types of oxygen species on the interaction of NO with Cu(111) were examined.

2. Experimental

All experiments were performed in a home-made ultrahigh vacuum (UHV) chamber with a base pressure of 2.0×10^{-8} Pa. The UHV chamber was equipped with facilities for XPS, low electron energy diffraction (LEED), and differentially-pumped TPD measurements. The Cu(111) single crystal purchased from MaTeck was mounted on the sample holder by two Ta wires spot-welded to the back side of the sample. The sample temperature was monitored by a chromel-alumel thermocouple spot-welded to the backside of the sample and could be controlled between 110 and 1000 K. Prior to the experiments, the

Cu(111) sample was cleaned by repeated cycles of Ar ion sputtering and annealing until LEED gave a sharp (1×1) diffraction pattern and no contaminants could be detected by XPS.

NO (> 99.9999%, Arkonic Gases & Chemicals Inc.) was used as received and the purity was further confirmed by quadrupole mass spectrometry (QMS) prior to experiments. NO was dosed by a line-of-sight stainless steel doser (diameter: 8 mm) positioned ~ 2 cm in front of the Cu(111) surface. The NO exposures are reported herein without considering calibration for the enhancement effect of the doser. All exposures were reported in Langmuir ($1 \text{ L} = 1.33 \times 10^{-4} \text{ Pa}\cdot\text{s}$) without corrections for the gauge sensitivity.

During TPD experiments, the Cu(111) surface was positioned ~ 1 mm away from the collecting tube of a differential-pumped QMS. The heating rate was 2 K/s. The signals with $m/e = 30$ (NO), 44 (N_2O and CO_2), 28 (N_2 and CO), and 14 (N_2O , NO, N_2) were monitored. XPS spectra were recorded by a hemispherical energy analyzer (PHBIO 100 MCD, SPECS GmbH) with a pass energy of 20 eV using Al K_α radiation ($h\nu = 1486.6$ eV). All the O 1s XPS spectra were fitted to Gaussian-Lorentzian functions using XPS Peak 4.1 after subtracting the sloping background caused by the tail of the copper LMM Auger peak [28].

3. Results and discussion

3.1. NO adsorption on clean Cu(111)

Figure 1 displays XPS spectra obtained after Cu(111) was exposed to various amounts of NO at 115 K. Exposure of 0.001 L NO leads to two features at 399.0 eV (α -species) and 401.3 eV (β -species) in the N 1s spectra. Correspondingly, two O 1s peaks can be resolved with the binding energy of 531.0 and 532.6 eV, respectively. With increasing NO exposure, the peak positions of the two N-containing species were remained nearly unchanged, but the relative intensity ratio of α -species to β -species underwent a gradual decrease with NO exposure. The β -species becomes dominant at a high NO exposure of 0.02 L. In the O 1s spectra, at a NO exposure of 0.005 L, the intensity of the O 1s feature at 531.0 eV was largely enhanced and was accompanied by the development of a new O 1s peak at 528.7 eV.

Fig. 1. N 1s (a) and O 1s (b) XPS spectra after Cu(111) exposed to various amounts of NO at 115 K.

Increasing the NO exposure induces a further increase in the intensity of the latter O-species and an upward shift of the binding energy from 528.7 to 529.5 eV. As shown in previous investigations, NO adsorption on Cu(111) even at 85 K will produce $\text{N}_2\text{O}(\text{a})$ and $\text{O}(\text{a})$ at low temperatures, while the desorption temperature of the former is around 110–120 K [9,10,13,19,21]. The presence of $\text{N}_2\text{O}(\text{a})$ on Cu(111) is usually evidenced by N 1s features at 402 and 406 eV, as well as an O 1s peak at 535 eV [9], which were not observed in our case. Furthermore, the presence of atomic N(a) can be also ruled out due to the absence of a N 1s feature around 397 eV [27,29]. Therefore, at the 115 K temperature in the present study, NO will adsorb and produce $\text{N}_2\text{O}(\text{a})$ and $\text{O}(\text{a})$; once formed the $\text{N}_2\text{O}(\text{a})$ species will desorb from the surface, leaving $\text{O}(\text{a})$ on the surface. As $\text{O}(\text{a})$ accumulates, some $\text{NO}(\text{a})$ can adsorb molecularly. Therefore, the two observed N 1s peaks should correspond to two different NO adsorption states. Previous investigation shows that the N 1s feature at 399.0 eV appears first, followed by the N 1s signal at 401.3 eV as NO coverage increases. The two species are ascribed to “bent” and “linear” $\text{NO}(\text{a})$ species [9]. Since the latter dominates with increasing NO exposure (also $\text{O}(\text{a})$ coverage due to NO adsorption), the N 1s feature at 399.0 eV is assigned to the $\text{NO}(\text{a})$ molecular state while that at 401.3 eV is assigned to $\text{NO}(\text{a})$ interacting with the neighboring $\text{O}(\text{a})$. The assignment is also supported by the following results of NO adsorption on O-precovered surfaces. The O 1s peak at 531.0 eV is related to $\text{NO}(\text{a})$ adsorbed at multiple sites, similar to the case of $\text{NO}/\text{Ag}(111)$ [9,30]. The O 1s feature at 532.6 eV may also result from $\text{NO}(\text{a})$ since its intensity is diminished upon NO desorption in the following annealing experiments. Therefore, the O 1s peaks at 531 and 532.6 eV are tentatively explained by $\text{NO}(\text{a})$ adsorbed at different sites. Similar results are also reported for NO adsorption on $\text{Pt}(111)$ at 110 K [31]. While $\text{NO}(\text{a})$ adsorbed at fcc-hollow and top sites exhibits a single N 1s peak at 400.4 K, two O features are observed at 532.0 and 530.3 eV, respectively, in the corresponding O 1s spectra [31]. The other O 1s features at 528.7 and 529.5 eV correspond to different surface oxygen species and their assignments will be discussed later.

The NO ($m/e = 30$), N_2O ($m/e = 44$), and N_2 ($m/e = 28$) signals are observed as desorption products in the TPD spectra

from Cu(111) after NO exposure at 115 K. The TPD results after a surface exposure of 0.005 L NO on Cu(111) are shown in Fig. 2(a). Note that the Cu substrate cleaning procedure was carried out before each NO exposure during TPD measurements since NO adsorption and desorption on Cu(111) will form $\text{O}(\text{a})$ on the surface. Two NO desorption peaks were observed at 150 and 130 K. Both N_2O and N_2 desorption occurs with almost identical peak shapes and desorption temperatures to that of NO. In the above XPS results, there is no evidence for the presence of $\text{N}_2\text{O}(\text{a})$ and N(a) species after NO adsorption at 115 K (Fig. 1). In fact, after its formation upon NO adsorption at the low temperature of 88 K, the desorption of $\text{N}_2\text{O}(\text{a})$ was reported to be around 110–120 K [21]. Together, this data strongly suggests that both N_2O and N_2 come from the thermal dissociation of adsorbed NO upon heating [13]. Two possible mechanisms have been proposed for the formation of N_2O during NO desorption: one is the interaction of $\text{NO}(\text{a})$ with N(a) produced by NO dissociation upon heating and the other is via the decomposition of a $(\text{NO})_2$ dimer intermediate [9,10,13,17,19, 21,25]. The presence of $(\text{NO})_2$ dimers has been confirmed on Cu surface at low temperatures by vibrational spectroscopy [17,21,25]. For N_2 desorption signal, it must come from the dissociation of the N_2O desorption product because the recombinative desorption of N(a) was observed to be above 500 K on Cu(111) [32]. The amu 28 signal observed at 196 K is assigned to CO contamination from the background. Its coverage was estimated to be below 0.01 ML by comparing the desorption peak area with that of saturated CO ($\theta_{\text{sat}} \sim 0.44$ ML [33]), and such small amounts of CO do not affect NO adsorption on Cu(111) [13].

Figures 2(b–d) show a series of TPD profiles of NO, N_2O , and N_2 signals obtained after Cu(111) was exposed to various amounts of NO at 115 K. At 0.001 L exposure, one NO desorption peak is dominant at 150 K with a shoulder at 140 K. Both desorption maximums shift to lower temperatures while the shoulder peak increases in intensity quickly with increasing NO exposure to 0.005 L. Upon further increasing the NO exposure, all the N-containing desorption signals are suppressed because of oxygen accumulation on the surface left by NO dissociative adsorption ($\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}(\text{g}) + \text{O}(\text{a})$), which blocks the surface for subsequent NO adsorption [9,10,13,19]. At exposure of 0.01

Fig. 2. (a) TPD profiles for NO, N_2O , and N_2 from Cu(111) after exposure to 0.005 L NO at 115 K. TPD profiles of NO ($m/e = 30$) (b), N_2O ($m/e = 44$) (c), and N_2 ($m/e = 28$) (d) from Cu(111) after various exposure of NO at 115 K.

L, only one desorption peak appears at 136 K for all three desorption products in the TPD profiles. Exposure of 0.02 L NO results in the appearance of broad desorption peaks at 130 and 170 K, along with a tiny peak at 270 K. Above 0.02 L, the surface is saturated by NO and the TPD results are unchanged at higher NO exposures of 0.05 L. Our TPD results at low NO exposures are generally consistent with previous work, which showed NO desorption at 106 and 140 K after NO saturation on Cu(111) at an even low temperature of 80 K [13]. On the basis of TPD and HREELS results, the authors assigned the two NO desorption peaks to the desorption of atop and bridge adsorbed NO, respectively [13]. Here we adopt the same assignments. At NO exposures above 0.01L, the situation is different. Since the adsorption temperature of NO in the present study (115 K) is relatively higher than the previous study (80 K) [13], it is expected that the surface is covered by NO(a) and O(a) as indicated by our XPS results (Fig. 1). Therefore, the desorption peak at 170 K at higher NO exposure is ascribed to NO(a) stabilized by coadsorbed O(a), which will be discussed below. This adsorbed state is evidenced by the N 1s feature at 401.3 eV and the O 1s peak at 531.0 eV (Fig. 1).

Figure 3 shows the XPS spectra after Cu(111) exposure of 0.001 L NO at 115 K, followed by annealing at various temperatures. In the N 1s region, the two NO(a) species (α and β species), which were observed at 399.0 and 401.3 eV after NO exposure of 0.001 L at 115 K, disappear completely upon heating the surface to 180 K. Above that temperature, there are no N-containing species present on the surface, corresponding to the complete desorption of species such as NO, N₂O, and N₂ below 180 K in the TPD profiles (Fig. 2). In the region of O 1s, the O 1s state located at 532.5 eV attenuates largely, implying that it is related to NO(a) state. The O 1s feature at 531 eV (denoted as O₅₃₁) increases in intensity with annealing temperature of 180 K. Since no N-related adsorbates are present on the surface at this temperature, the O 1s peak at 531.0 eV exclusively comes from atomic oxygen species which were formed by the NO dissociative desorption producing N₂O(g) and N₂(g) (Fig. 2) [28,29,34]. Further heating of the surface to 265 K led to a decrease in the intensity of the O 1s peak while its binding energy remained almost constant. At an annealing temperature

of 350 K, another O 1s feature started to appear at 529.6 eV (denoted as O₅₂₉) accompanied by further attenuation of the O₅₃₁ state. The assignment of different O 1s components on Cu(111) is still controversial in the literature. The O₅₂₉ state was usually observed when Cu(111) was exposed to O₂ at room temperature and was assigned to chemisorbed oxygen species at 3-fold hollow sites [8,29,35,36]. The O₅₃₁ state was observed after NH₃-precovered Cu(111) was exposed to O₂ at 85 K and was assigned to subsurface oxygen [28,29]. However, Bloch et al. [34] found that such oxygen species are easily removed by Ar⁺ sputtering, indicating a surface oxygen species. By HREELS, the $\nu(\text{Cu-O})$ mode was observed near 370 cm⁻¹ upon O₂ exposure over a temperature range of 100–230 K, while it shifts to 240–260 cm⁻¹ when O₂ exposure is performed at temperature between 300 and 450 K, implying the presence of two different chemisorbed oxygen species on the Cu(111) surface depending on the exposure temperature [13,35,37]. Here, we assign the O₅₃₁ state appearing at low O(a) coverage upon low temperature NO adsorption to the chemisorbed oxygen species adsorbed at lower coordination sites (bridge sites or atop sites) [35]. The appearance of the O 1s state at 529.6 eV at the expense of O₅₃₁ above 265 K indicates a transformation between the two different chemisorbed oxygen species, supporting the above assignment. No oxygen state was detected when the surface temperature was increased to 650 K, probably because of oxygen diffusion into the bulk copper substrate [34].

The type of oxygen species changes largely when increasing the initial NO exposure on Cu(111) followed by annealing at high temperature. Figure 4 shows the XPS spectra of Cu(111) after exposure to 0.01 L NO at 115 K and subsequent annealing. In the N 1s region, the α -species (N 1s BE of 399.0 eV) completely disappears at an annealing temperature of 150 K while the intensity of the β -species (N 1s BE of 401.3 eV) diminishes. This indicates that the β -species (O-interacting NO(a)) adsorbs more strongly on Cu(111) than the α -species (NO(a)). At a higher temperature of 240 K, the N-related species desorb completely from the surface, consistent with the TPD results (Fig. 2). In the case of the O 1s feature, three O 1s peaks were resolved, located at 529.0, 531.0, and 532.7 eV. With increasing annealing temperature, the O 1s feature at 532.7 eV disappears

Fig. 3. N 1s (a) and O 1s (b) XPS spectra obtained after Cu(111) was exposed to 0.001 L NO at 115 K followed by annealing to indicated temperature.

Fig. 4. N 1s (a) and O 1s (b) XPS spectra obtained after Cu(111) was exposed to 0.01 L NO at 115 K followed by annealing to indicated temperature.

due to desorption of adsorbed NO, supporting its assignment to adsorbed NO(a) molecules. The O 1s peak located at 529.0 eV was previously observed in a coadsorbed layer of $\text{NH}_3\text{-O}_2$ and $\text{NH}_3\text{-NO}$ on Cu(111) and was assigned to metastable atomic oxygen [28,29]. The O 1s feature at 529.0 eV shifts to higher binding energy and increases in intensity, suggesting a transformation from a metastable oxygen species to a chemisorbed oxygen species. At the same time, the O 1s state at 531.0 eV loses intensity, accompanied by an increase in the intensity of the chemisorbed oxygen species (O_{529} state) at higher temperature, similar to the case of low NO exposure (Fig. 3(b)). Upon annealing at 650 K, the surface is exclusively covered by chemisorbed oxygen species at 529.8 eV.

3.2. NO adsorption on O-precovered Cu(111)

The above NO adsorption-annealing experiments clearly indicate that at least three different oxygen species exist on Cu(111) and that transformations between these different oxygen species occur by varying the NO exposure and annealing temperature. Therefore, this method provides a facile way to

prepare various oxygen species and examine their reactivities on the copper substrate. In the following section, two different chemisorbed oxygen species (O_{531} and O_{529}) were produced on the surface and their roles in the NO adsorption behavior were examined by XPS and TPD. The oxygen coverage values in the present study were calibrated by comparing the intensity of the O 1s XPS spectra to that of an O-saturated surface ($\theta_{\text{sat}} \sim 0.27$ ML) which was prepared by oxygen exposure at room temperature [38,39].

First, NO adsorption on O_{531} -preadsorbed Cu(111) was studied by XPS and TPD. To prepare the O_{531} species, Cu(111) was exposed to 0.001 L NO at 115 K, followed by heating the surface to 220 K to remove the N-containing species (Fig. 3). This treatment can be repeated several times to obtain various O(a) coverages. The XPS spectra of the resultant O-covered surfaces are shown in Fig. 5(a). For all the presented O(a) coverages, the chemisorbed O_{531} species are dominant on the surface, although there are small contributions from other O 1s features at 529.4 and 532.5 eV at higher O(a) coverage. Figures 5(b) and 5(c) show the observed N 1s XPS spectra and O 1s difference spectra after the O_{531} -precovered Cu(111) surfaces

Fig. 5. (a) O 1s XPS spectra after Cu(111) was covered with various amount of chemisorbed O_{531} species by repeated cycles of NO adsorption and annealing to 220 K. (b) N 1s spectra and (c) O 1s difference spectra after the O_{531} -precovered Cu(111) surfaces in (a) were exposed to 0.001 L NO at 115 K.

were further exposed to 0.001 L NO at 115 K. Similar to the clean surface, there are two N 1s states observed at 399.0 and 401.3 eV on the O₅₃₁-precovered Cu(111). The former peak is assigned to NO(a) adsorbed at sites far from O(a) species (α -NO species), and the latter to NO(a) species interacting with O(a) (β -NO species). With increasing O(a) coverage, the α -NO species signal decreased gradually and the β -NO species signal remained almost constant. The presence of O₅₃₁ species affects the relative occupation of α -NO and β -NO species; almost no NO(a) adsorbs on O(a)-saturated surfaces ($\theta = 0.50$ ML). In the O 1s difference spectra, the O 1s feature at 531 eV which appears after NO adsorption on Cu(111) at lower O(a) coverages corresponds to the adsorption of NO(a) and the formation of O(a) (Fig. 3). At an oxygen coverage of 0.28 ML, the O 1s peak at 531.0 eV is replaced by an O 1s feature near 530 eV, probably related to an O species in an O-NO complex. At the O(a) saturation coverage of 0.5 ML, the absence of any O 1s feature induced by NO adsorption again suggests that NO adsorption is completely blocked by the presence of O(a).

Figure 6(a) shows the TPD profiles obtained after Cu(111) was precovered with various amounts of chemisorbed O₅₃₁ species and further exposed to 0.001 L NO. The amu 14 signal is also shown in comparison to the amu 28 signal to differentiate the contribution from CO contamination desorption. Generally, all three N-containing molecules are observed as desorption products, NO, N₂O, and N₂ for all the oxygen-precovered Cu(111) surfaces. In most cases, NO, N₂O, and N₂ molecules show similar desorption peak shape and desorption temperatures. On the clean surface, the desorption temperature is about 154 K. With increasing O₅₃₁ coverage, the NO desorption peak shifts to lower temperatures, which can be explained by NO(a) shifting adsorption sites from multiple sites to top sites [13]. At an oxygen coverage of 0.28 ML, another desorption peak appears at 155 K and shifts to higher temperatures with further increases in oxygen coverage. This indicates the adsorbed NO species are stabilized by the oxygen species at higher O(a) coverages.

On the basis of the TPD results, in addition to simple molecular NO desorption from Cu(111), some NO(a) undergoes dissociative desorption producing N₂O(a) and O(a) on the surface.

However, further information is still needed to clarify whether the desorption process involves an (NO)₂ intermediate. The N₂O(a) species either desorbs from the surface or dissociates into N₂(g) and O(a) upon its formation. To further analyze the NO desorption behavior, following our previous investigation of NO adsorption on Pt(110) [40], the NO conversion and N₂ selectivity can be defined as follows:

$$\text{NO conversion} = \frac{2 \times [S(\text{N}_2) + S(\text{N}_2\text{O})]}{S(\text{NO}) + 2 \times [S(\text{N}_2) + S(\text{N}_2\text{O})]}$$

$$\text{N}_2 \text{ selectivity} = \frac{S(\text{N}_2)}{S(\text{N}_2) + S(\text{N}_2\text{O})}$$

where $S(\text{N}_2)$, $S(\text{N}_2\text{O})$, and $S(\text{NO})$ represents the integrated area of the N₂, N₂O, and NO TPD peaks, respectively. Here, we use the same rough approximation to examine the desorption process of NO. For NO desorption, the fragmentation of the amu 44 signal (30%) was subtracted from the amu 30 signal. For N₂ desorption, especially at higher O(a) coverage, the N₂ signal at amu 28 is disturbed by signal from CO. Therefore, the amu 14 signal was used for the above estimation after subtracting contributions from fragmentation of amu 44 (~13%) and amu 30 (~8%), and then the N₂ signal was estimated by the resultant amu 14 signal considering the fragmentation ratio (~13%) of amu 14 to amu 28 for N₂ in QMS. The results are shown in Fig. 7. For N₂ conversion, it is evident that almost all NO(a) molecules convert into N₂O and N₂ during NO desorption, independent of the O(a) coverage. Furthermore, the N₂ selectivity decreases gradually with increasing O(a) coverage, suggesting that O(a) suppresses dissociation of the N₂O intermediate, similar to the case of Pt(110) [40]. At O(a) saturation coverage, only N₂O is released as the NO(a) desorption product. The above results strongly suggest that chemisorbed O₅₃₁ species principally affect the dissociation of the N₂O(a) intermediate, but not NO conversion, except for a slight blocking effect.

The effect of another chemisorbed oxygen species (O₅₂₉ state) on NO adsorption on Cu(111) was also investigated. To prepare O₅₂₉ species, the Cu(111) surface was exposed to NO followed by annealing at 650 K. The oxygen coverage was controlled by varying the NO exposure. Figure 8(a) displays the O 1s XPS spectra of O₅₂₉-covered Cu(111). There is only a single peak at 529.7 eV which gains intensity with increasing O(a)

Fig. 6. TPD profiles of NO (a), N₂O (b), N₂ (c), and N₂ (d) following 0.001 L NO exposure on Cu(111) precovered with various coverage of chemisorbed O₅₃₁ species at 115 K.

Fig. 7. NO conversion and N₂ selectivity during NO desorption as a function of coverage of O₅₃₁-precovered Cu(111) substrates estimated from the TPD results in Fig. 6.

coverage. The N 1s spectra and O 1s difference spectra are recorded and displayed in Fig. 8(b) and (c) for O₅₂₉-precovered Cu(111) were further exposed to 0.001 L NO at 115 K. In the N 1s spectra, both α -NO species (BE at 399 eV) and β -NO species (BE at 401.3 eV) diminish in intensity as the O coverage increases, suggesting a strong blocking effect of O species. In contrast to the case of the O₅₃₁-precovered surfaces, the relative intensities of the α - and β -NO species are nearly constant with increasing O(a) coverage. This suggests a negligible effect of O₅₂₉ species on the adsorption state of NO(a). In the O 1s difference spectra (Fig. 8(c)), two O 1s features are detected at 531.0 and 532.5 eV for the clean and O₅₂₉-covered surfaces, which are ascribed to adsorbed NO(a) states with and without neighboring O(a). The former O 1s peak may also involve a contribution from chemisorbed O₅₃₁ species. As indicated by the N 1s spectra, the O 1s features are suppressed with increasing O coverage while the peak position and the relative intensity remain almost constant. At the O saturation coverage, only a small amount of NO adsorbs on the surface, evidenced by a tiny N 1s and O 1s signal in the XPS spectra.

Figure 9 displays a series of TPD profiles of NO, N₂O, and N₂ for exposure of O₅₂₉-precovered Cu(111) to 0.001 L NO at 115 K. The presence of O₅₂₉ species shows a stronger site-blocking effect than the O₅₃₁ species. At an O coverage of 0.11 ML, all of

the desorption signals decrease in intensity with a slight downward shift in the desorption temperature. When the O coverage was increased to 0.17 ML, all the desorption signals shifted to higher temperatures, and at the O saturation coverage of 0.27 ML, only the molecular NO desorption signal was observed, with no N₂O and N₂ signal detected. The amu 28 signal observed at around 140 K at an O(a) coverage of 0.27 ML is due to the desorption of background adsorbed CO, as indicated by the amu 14 signal in Fig. 9(d).

Similar analysis of the NO desorption process by estimation of the N₂ conversion and N₂ selectivity were also performed for the O₅₂₉-covered surface, and the results of this analysis are shown in Fig. 10. As the O₅₂₉ species coverage increases, NO conversion gradually decreases – in contrast to the case of O₅₃₁ species, which strongly indicates that dissociative NO desorption is suppressed by chemisorbed O₅₂₉ states. A similar effect of O₅₂₉ species on NO adsorption was also observed on other transition metal surfaces, such as Pt(111), Pt(110) and Ni(111) [40–43]. The suppression of NO dissociative desorption by O species can be explained by a reduced electron density in the NO 2 π^* antibonding orbital caused by NO interactions with coadsorbed electronegative oxygen atoms [26,40–43]. As to N₂ selectivity, the ratio is almost constant up to O coverages of 0.11 ML, but decrease sharply to zero at an O coverage of 0.17 ML. At the O₅₂₉ saturation coverage of 0.27 ML, only NO was observed as a desorption product, while only N₂O desorption was observed at the O₅₃₁ saturation coverage of 0.5 ML.

Our results clearly indicate that the effects of oxygen pre-coverage on the chemical properties of Cu(111) depend largely on the specific type of oxygen species and the O coverage. The O₅₃₁ and O₅₂₉ species show different effects on NO adsorption behavior. The O₅₃₁ species affects the adsorption states of NO(a) and shows a repulsive interaction with NO(a) (Fig. 5(b) and Fig. 6), while the O₅₂₉ species have no significant effect on the adsorption state as observed by XPS and TPD measurements (Figs. 8 and 9). Furthermore, in the presence of O₅₃₁ species, most adsorbed NO(a) molecules undergo dissociative desorption, similar to the clean surface case, while molecular desorption of NO was preferred when O₅₂₉ species were present.

Fig. 8. (a) O 1s XPS spectra after Cu(111) was covered with various amount of chemisorbed O₅₂₉ species by repeated cycles of NO adsorption and annealing to 650 K. (b) N 1s spectra and (c) O 1s difference spectra after the O₅₂₉-precovered Cu(111) surface was exposed to 0.001 L NO at 115 K.

Fig. 9. TPD profiles of NO (a), N₂O (b), N₂ (c), and N₂ (d) following 0.001 L NO exposure on O₅₂₉-precovered Cu(111) with various surface coverages at 115 K.

Fig. 10. NO conversion and N₂ selectivity during NO desorption as a function of surface coverage for the O₅₂₉-precovered Cu(111) estimated from the TPD results in Fig. 9.

A similar dependence of chemical properties on the types of oxygen species has been observed previously [28,44]. In that study, the reactivities of different oxygen species with O 1s binding energies of 531.3 and 529.8 eV have also been examined by comparing their ability to react with adsorbed NH₃ on Cu(111) at room temperature [28,44]. The results clearly indicated that the oxygen species at 529.8 eV could easily react with ammonia, while the species with O 1s BE of 531.3 eV is unaffected by the presence of NH₃ [28,44]. The present results provide a further understanding of the role of oxygen species in surface reactions on Cu surfaces.

4. Conclusions

On the basis of XPS and TPD results, the following conclusions can be made. At least three chemisorbed oxygen species were observed during NO adsorption on Cu(111), including a metastable O(a) species with an O 1s BE at 528.9 eV and two chemisorbed O(a) species with O 1s BEs of 529.5 and 531.0 eV. The O₅₂₈ and O₅₃₁ states can transform into the O₅₂₉ state at high oxygen coverage and at elevated surface temperature. When the surface is pre-covered by the O₅₃₁ species, most adsorbed NO(a) species dissociate into N₂O and N₂ during desorption. In contrast, dissociative desorption of NO(a) was largely suppressed in the presence of O₅₂₉ species. Furthermore, the O₅₂₉ species show a more significant blocking effect

toward NO adsorption than the chemisorbed O₅₃₁ species. Our results provide more information about the effect of oxygen species on the chemical properties of Cu surfaces, which depends largely on the type of oxygen species and oxygen coverage.

References

- [1] Szanyi J, Goodman D W. *Catal Lett*, 1993, 21: 165
- [2] Millar G J, Canning A, Rose G, Wood B, Trewartha L, Mackinnon I D R. *J Catal*, 1999, 183: 169
- [3] Yang Y X, Evans J, Rodriguez J A, White M G, Liu P. *Phys Chem Chem Phys*, 2010, 12: 9909
- [4] Yang F, Choi Y M, Agnoli S, Liu P, Stacchiola D, Hrbek J, Rodriguez J A. *J Phys Chem C*, 2011, 115: 23062
- [5] Gao Z M, Zhou M, Deng H, Yue Y. *J Nat Gas Chem*, 2012, 21: 513
- [6] Cao J L, Wang Y, Ma T Y, Liu Y P, Yuan Z Y. *J Nat Gas Chem*, 2011, 20: 669
- [7] Salmeron M, Schlögl R. *Surf Sci Rep*, 2008, 63: 169
- [8] Johnson D W, Matloob M H, Roberts M W. *J Chem Soc, Chem Comm*, 1978: 40
- [9] Johnson D W, Matloob M H, Roberts M W. *J Chem Soc, Faraday Trans*, 1979, 75: 2143
- [10] Wendelken J F. *J Vac Sci Technol*, 1982, 20: 884
- [11] Balkenende A R, Gijzeman O L J, Geus J W. *Appl Surf Sci*, 1989, 37: 189
- [12] Balkenende A R, den Daas H, Huisman M, Gijzeman O L J, Geus J W. *Appl Surf Sci*, 1991, 47: 341
- [13] So S K, Franchy R, Ho W. *J Chem Phys*, 1991, 95: 1385
- [14] Balkenende A R, Hoogendam R, de Beer T, Gijzeman O L J, Geus J W. *Appl Surf Sci*, 1992, 55: 1
- [15] Fernández-García M, Conesa J C, Illas F. *Surf Sci*, 1993, 280: 441
- [16] Wee A T S, Lin J, Huan A C H, Loh F C, Tan K L. *Surf Sci*, 1994, 304: 145
- [17] Brown W A, Sharma R K, King D A, Haq S. *J Phys Chem*, 1996, 100: 12559
- [18] Illas F, Ricart J M, Fernandez-Garcia M. *J Chem Phys*, 1996, 104: 5647
- [19] Sueyoshi T, Sasaki T, Iwasawa Y. *J Phys Chem*, 1996, 100: 13646
- [20] van Daelen M A, Li Y S, Newsam J M, van Santen R A. *J Phys Chem*, 1996, 100: 2279
- [21] Dumas P, Suhren M, Chabal Y J, Hirschmugl C J, Williams G P. *Surf Sci*, 1997, 371: 200
- [22] Carley A F, Davies P R, Harikumar K R, Jones R V, Kulkarni G U, Roberts M W. *Top Catal*, 2000, 14: 101
- [23] Carley A F, Davies P R, Harikumar K R, Jones R V, Kulkarni G U, Roberts M W. *Top Catal*, 2001, 14: 101
- [24] Bogicevic A, Hass K C. *Surf Sci*, 2002, 506: L237

Graphical Abstract

Chin. J. Catal., 2013, 34: 964–972 doi: 10.1016/S1872-2067(12)60585-3

XPS and TPD study of NO interaction with Cu(111): Role of different oxygen species

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The adsorption and reaction behavior of NO on Cu(111) largely depends on the type of precovered oxygen species, which were prepared by varying NO exposure and annealing temperature.

- [25] Kim C M, Yi C W, Goodman D W. *J Phys Chem B*, 2002, 106: 7065
 [26] Yen M-Y, Ho J-J. *Chem Phys*, 2010, 373: 300
 [27] Matloob M H, Roberts M W. *J Chem Soc, Faraday Trans*, 1977, 73: 1393
 [28] Davies P R, Roberts M W, Shukla N, Vincent D J. *Surf Sci*, 1995, 325: 50
 [29] Davies P R, Shukla N, Vincent D J. *J Chem Soc, Faraday Trans*, 1995, 91: 2885
 [30] Behm R J, Brundle C R. *J Vac Sci Technol, A*, 1984, 2: 1040
 [31] Zhu J F, Kinne M, Fuhrmann T, Denecke R, Steinrück H P. *Surf Sci*, 2003, 529: 384
 [32] Skelly J F, Bertrams T, Munz A W, Murphy M J, Hodgson A. *Surf Sci*, 1998, 415: 48
 [33] Kirstein W, Krüger B, Thieme F. *Surf Sci*, 1986, 176: 505
 [34] Bloch J, Bottomley D J, Janz S, van Driel H M, Timsit R S. *J Chem Phys*, 1993, 98: 9167
 [35] Sueyoshi T, Sasaki T, Iwasawa Y. *Surf Sci*, 1996, 365: 310
 [36] Wiame F, Maurice V, Marcus P. *Surf Sci*, 2007, 601: 1193
 [37] Dubois L H. *Surf Sci*, 1982, 119: 399
 [38] Moritani K, Okada M, Sato S, Goto S, Kasai T, Yoshigoe A, Teraoka Y. *J Vac Sci Technol A*, 2004, 22: 1625
 [39] Moritani K, Okada M, Teraoka Y, Yoshigoe A, Kasai T. *J Phys Chem C*, 2008, 112: 8662
 [40] Jiang Z Q, Huang W X, Tan D L, Zhai R S, Bao X H. *Surf Sci*, 2006, 600: 4860
 [41] Zhu J F, Kinne M, Fuhrmann T, Trankenschuh B, Denecke R, Steinrück H P. *Surf Sci*, 2003, 547: 410
 [42] Root T W, Fisher G B, Schmidt L D. *J Chem Phys*, 1986, 85: 4687
 [43] Chen J G, Erley W, Ibach H. *Surf Sci*, 1989, 224: 215
 [44] Davies P R, Bowker M. *Catal Today*, 2010, 154: 31

NO在Cu(111)表面吸附和分解的XPS和TPD研究：不同氧物种的影响

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摘要: 利用X射线光电子能谱和程序升温脱附谱研究了NO在清洁和预吸附氧的Cu(111)表面上的吸附和反应。通过改变NO的暴露量和退火温度, 在Cu(111)表面可以制备出不同种类的化学吸附氧物种, 其O 1s的结合能分别位于531.0 eV (O₅₃₁)和529.7 eV (O₅₂₉)。表面O₅₃₁物种的存在对NO的不同吸附状态有着显著影响, 同时使得大部分NO吸附分子(NO(a))在加热过程中发生分解并以N₂O和N₂形式脱附; 而表面O₅₂₉物种对NO(a)的解离脱附有着明显的抑制作用。相对于O₅₃₁物种来说, O₅₂₉物种对NO吸附表现出更强的位阻效应。上述结果表明, NO在Cu(111)表面的吸附和分解行为与预吸附氧物种的种类和覆盖度密切相关。

关键词: 一氧化氮; Cu(111)表面; 氧物种; 吸附; X射线光电子能谱; 程序升温脱附谱

收稿日期: 2013-01-05. 接受日期: 2013-02-04. 出版日期: 2013-05-20.

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基金来源: 国家自然科学基金(21073172); 国家重点基础研究发展计划(973计划, 2013CB933104, 2013CB933102, 2010CB923301); 中央高校基本科研业务费专项资金资助。

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