Interaction of metal with oxide films: V on Cr_2O_3(0001)/Re(0001) and Cr on V_2O_3(0001)/Re(0001)

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Abstract
The interactions of V with Cr_2O_3(0001) films and Cr with V_2O_3(0001) films at room temperature are studied using x-ray photoelectron spectroscopy and low-energy-electron diffraction. The results show that the deposited V is oxidized and the Cr_2O_3(0001) surface is reduced at the initial coverage due to the interaction of V with the Cr_2O_3 substrate; V becomes metallic at V coverage greater than 5 monolayer equivalent. Full oxidization of the deposited vanadium cannot be achieved by O_2 exposure at room temperature for 20 min. However, V_2O_3(0001) films have been observed after heating the sample to 600–700 K in oxygen ambient at 1×10^{-7} mbar. Similar results have been obtained for the Cr/V_2O_3(0001)/Re(0001) system.

1. Introduction

Due to the wide applications of metal/metal oxide in various industries, for example gas sensors, microelectron devices, catalysts, corrosion protection and so on, much attention has been devoted to the studies of their interfaces. Although the metal/oxide interaction is influenced by a variety of factors, such as defects, impurities and formation of complex mixed oxide phases, it is generally accepted that the strength of the metal/oxide interaction is controlled by the oxygen affinity of the metal interacting with the oxide surface; i.e., the more negative the heat of oxide formation of the deposited metal, the stronger the interaction with the oxide [1]. To aid in the understanding of the physics and chemistry of the metal/oxide interface, well ordered ultrathin oxide films have been investigated as model samples instead of bulk oxide surfaces in recent years in order to use various electron spectroscopes while overcoming surface charging and sample heating problems [2].

Chromium oxide is widely used as a catalyst and anti-corrosive material. Vanadium oxide, supported on TiO_2 or Al_2O_3, is also an important heterogeneous catalyst commonly used for

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the selective reduction of NO with NH$_3$ and the selective oxidation of hydrocarbons. In these applications, low-chemical-state Cr and V usually play important roles, and many Cr/oxide and V/oxide systems have been studied. However, few studies have addressed the interaction of the system of V/Cr$_2$O$_3$ or Cr/V$_2$O$_3$, even though both systems are very interesting because both V and Cr have strong affinities for O, resulting in competition for lattice O^{2-} ions.

In previous work, using the same substrate, Re(0001), we have successfully prepared well ordered ultrathin chromium oxide films [3] and vanadium oxide films [4]. In this work, we study the interaction and oxidation of vanadium on Cr$_2$O$_3$(0001) films and chromium on V$_2$O$_3$(0001) films by means of x-ray photoelectron spectroscopy (XPS) and low-energy-electron diffraction (LEED).

2. Experimental details

The experiments are carried out in an ESCALAB-5 system made by VG Scientific, which has two ultrahigh-vacuum (UHV) chambers; both have base pressure of 2×10^{-9} mbar. One of the chambers (the analysis chamber) is equipped with reverse-view optics for LEED, dual-anode x-ray sources (Mg and Al), and a hemispherical analyser (radius = 100 mm, slit = 10×4 mm^2) for XPS. In the other chamber (preparation chamber), there is an Ar$^+$ sputtering gun, metal sources and sample heater. The sample is prepared in the preparation chamber and analysed in the analysis chamber.

The Re(0001) sample (10 mm diameter disc with a thickness of 1.0 mm) is spot welded to a Mo holder with Ta slivers, allowing electron bombardment heating to 2500 K. A W–5%Re/W–26%Re thermocouple is spot welded near to the sample for temperature monitoring. The surface is prepared by Ar$^+$ bombardment at 5 keV, followed by annealing in $\sim 10^{-7}$ mbar O$_2$ at about 1200 K, with a subsequent flash to 2000 K in vacuum. After several cyclic treatments, no impurity is detected by XPS and a clear hexagonal LEED pattern appears.

The vanadium doser consists of a vanadium wire wrapped tightly around a tungsten filament, and the chromium source is made from an irregular chromium block (<3 mm in size) which is tightly wrapped around with a tungsten filament. Both the Cr and V sources are 99.9% pure. Prior to the deposition of Cr and V, the V$_2$O$_3$(0001) and Cr$_2$O$_3$(0001) films on the Re(0001) are prepared respectively, as documented in our previous works [3, 4]. The deposition rates of Cr and V are about 0.2 and 0.3 monolayers (ML) min^{-1}, respectively, calibrated via XPS of V 2p and Cr 2p deposited onto the Re(0001) surface as a function of deposition time. Since Cr (or V) is not necessarily grown on the oxide films layer by layer, we prefer to use the monolayer equivalent (MLE) as a measurement for Cr and V coverage.

The XPS analyses are performed using a Mg K$\alpha_{1,2}$ x-ray source (1253.6 eV) without a monochromator and a pass energy of 50 eV is used while collecting all data. Binding energies (BEs) are calibrated with respect to the pure bulk Au 4f$_{7/2}$ (BE = 84.0 eV) and Cu 2p$_{3/2}$ (BE = 932.7 eV) features. All data are recorded at room temperature (RT).

3. Results and discussion

3.1. Interaction between V and Cr$_2$O$_3$(0001) film

Figure 1 shows the XP spectra of the O 1s and V 2p region, collected from a clean Cr$_2$O$_3$(0001) film and after the successive deposition of submonolayer-to-multilayer amounts of vanadium. An increase of V 2p line intensity, accompanied by a simultaneous continuous shift toward lower BE with increase of V deposition, is observed. In the submonolayer coverage regime, the V 2p lines shift toward higher BE, indicating the oxidation of vanadium. The development
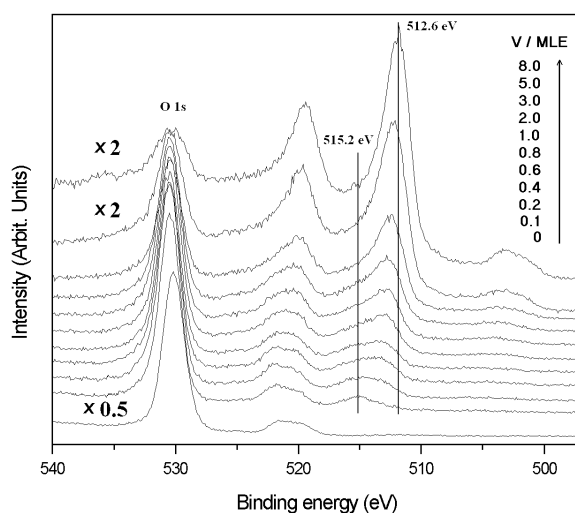
Figure 1. XPS of V 2p and O 1s as a function of vanadium coverage.

of the line-shape with increasing vanadium coverage shows that the V $2p_{3/2}$ photoemission signal has a shoulder centred at 515.2 eV. It is well known that the V $2p_{3/2}$ core-level BEs for bulk V_2O_5, VO_2, V_2O_3, VO and metallic V are 516.9, 516.2, 515.7, 515.1 and 512.2 eV, respectively [5–11], so the broad features at 515.2 eV at coverage of 0.1 MLE vanadium in the present work can be attributed to V^{3+} or V^{2+} cations at the interface. The peak of V $2p_{3/2}$ at 512.6 eV, gradually becoming dominant at the vanadium coverage above 1 MLE, reveals that most of the vanadium on the substrate is metallic with part of the vanadium in an oxide state. At coverage greater than 5 MLE, vanadium becomes entirely metallic.

We also notice that the BE of O 1s shifts slightly to higher BE after V deposition. Since adatoms on insulators or intrinsic semiconductors usually cause Fermi level movement and result in an identical shift of the whole spectrum, this slight shift of O 1s is possibly due to the Fermi level movement induced by V. At higher coverage of V, the BE of O 1s basically remains unchanged even at very high vanadium thickness. This is perfectly reasonable since the BEs of O 1s for V_2O_3 and Cr_2O_3 are very close, and both V–O and Cr–O bond exist on the interface. The obvious peak attributed to O 1s at vanadium coverage of 8 MLE still can be seen in figure 1, but no line attributed to Cr 2p can be observed in the corresponding XP spectrum with the same vanadium coverage, as shown in figure 2. This is most likely due to the residual oxygen. However, the oxidation of the deposited vanadium cannot be attributed to this oxygen, otherwise the BE of V $2p_{3/2}$ would shift to a high value instead of 512.6 eV (see figure 1), the value of the metal. Furthermore, no BE shift of V 2p is observed when vanadium deposition on a clean Re(0001) surface is carried out under the same conditions (not shown here). It is therefore concluded that the oxidation of vanadium is a result of interaction with the Cr_2O_3 substrate.

One interesting result is that the oxidation of vanadium causes a reduction of chromium, as shown in figure 2. With increasing vanadium deposition (from top to bottom), the peak of Cr^{3+} cations becomes broader and a shoulder at 575.3 eV can be observed. Since the Cr $2p_{3/2}$ core level BEs are 576.7 eV for Cr^{3+}, 576.0 eV for Cr^{2+} and 574.2 eV for metallic chromium in the system of chromium oxide on Cu(100) [11, 12], the reduced Cr cations must be in the low-oxidation chemical states of Cr^{2+} and metallic chromium. Both the oxidation of vanadium and the reduction of Cr^{3+} cations on the substrate indicate charge transfer at the interface.
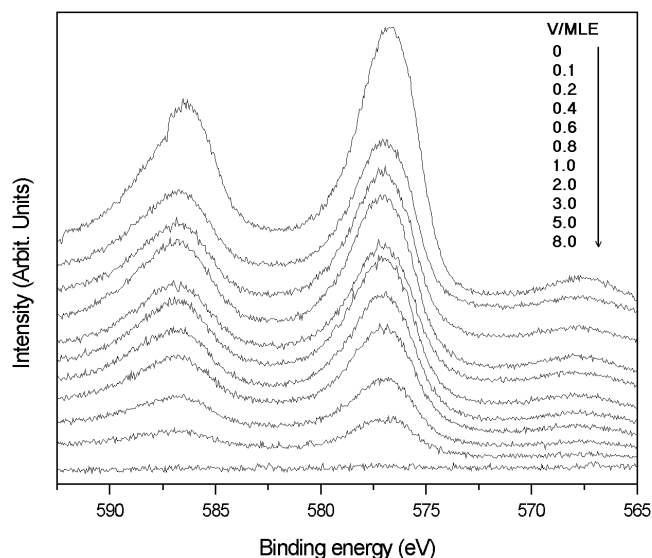
Figure 2. XPS of Cr 2p as a function of vanadium coverage.

A hexagonal LEED pattern is obtained from the clean $Cr_2O_3(0001)$ surface. However, when vanadium deposition is carried out step by step, the LEED pattern becomes obscure and disappears rapidly, indicating that the deposited vanadium is disordered on the $Cr_2O_3(0001)$ surface. Annealing treatment in vacuum leads to further chemical reaction between V and the $Cr_2O_3(0001)$ substrate, causing the BE of V 2p to shift to 514.1 eV, which is an indication of V_xO_y (the XP spectra are not shown here). However, no improved LEED pattern has been observed after annealing.

3.2. Oxidation of V on Cr2O3(0001) film

The oxidation is carried out on the surface with V coverage of 8 MLE. On this surface, no Cr 2p signal can be seen. Figure 3(b) shows the XPS result after the sample has been exposed to O_2 at 1×10^{-7} mbar for 10 min at RT. A peak with BE of 515.5 eV becomes dominant. This clearly indicates that part of the vanadium has been oxidized to V^{3+}. Further O_2 exposure for 20 min could not fully oxidize all the vanadium at RT (a shoulder at 512.6 eV can still be observed, as seen in figure 3(c)). However, it can be achieved by O_2 exposure of a hot sample at 600–700 K for 5 min as shown in figure 3(d). The BEs for O 1s and V $2p_{3/2}$ are 530.4 and 515.5 eV, respectively. These suggest the formation of V_2O_3 compared with reported BEs of O 1s and V $2p_{3/2}$ for different vanadium oxides [5–11]. After several annealing treatments in oxygen ambient, a hexagonal LEED pattern can be observed (not shown here). Since no Cr signal can be detected by XPS, it is believed that an ordered binary oxide film of $V_2O_3(0001)$ on $Cr_2O_3(0001)$ is prepared on the Re(0001) surface.

It is very interesting to point out that the BE of O 1s before O_2 exposure (see figure 3(a)) is a little higher than that after oxidation (see figures 3(b)–(d)). As we have discussed previously, this peak is assigned to the residual oxygen; the higher BE, therefore, indicates that the residual oxygen is in a chemical state different from that of V_2O_3. This coincides with our former argument that the oxidation of the deposited vanadium is the result of the interface interaction, instead of the residual oxygen.
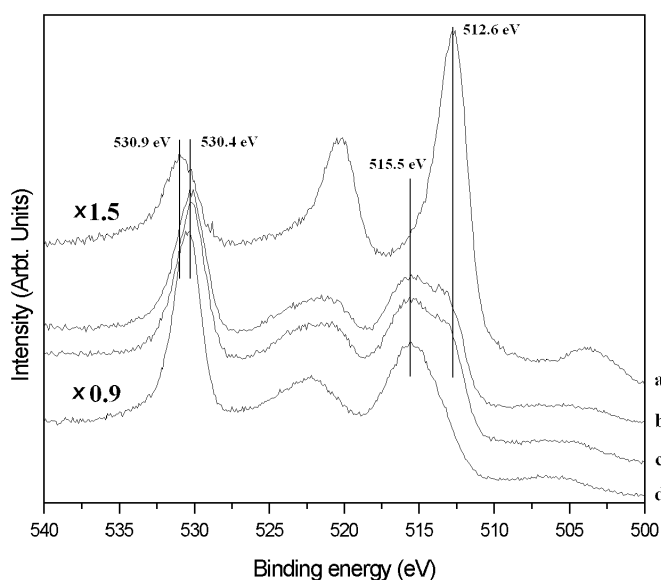
Figure 3. XPS of V 2p and O 1s in different oxidizing conditions. (a) Metallic vanadium with a thickness of 8 MLE; (b) after exposure to oxygen at RT for 10 min (1 × 10^{-7} mbar O$_2$); (c) after exposure to oxygen at RT for 20 min (1 × 10^{-7} mbar O$_2$); (d) after exposure to oxygen at 600–700 K for 5 min (1 × 10^{-7} mbar O$_2$).

3.3. Interaction between Cr and V$_2$O$_3$(0001) film

For a comparison, the interaction of chromium and the V$_2$O$_3$(0001) surface has also been studied. The XP spectra of Cr 2p are shown in figure 4. Initially, at the Cr coverage of 0.1 MLE, the peak of Cr 2p$_{3/2}$ centres at 576.3 eV. With coverage increased to 1 MLE, another peak at 574.3 eV gradually increases in intensity and becomes dominant. Compared with the values of Cr 2p$_{3/2}$ BE reported in the literature for Cr^{3+} (576.9 eV), Cr^{2+} (576.0 eV) and metallic Cr (574.2 eV) [11, 12], the peak of Cr 2p$_{3/2}$ at 576.3 eV is evidence of the formation of Cr^{3+} or Cr^{2+} cations at the interface. At higher chromium coverage from 1 to 3 MLE, a peak at 574.3 eV with a broad shoulder on the higher-BE side can be observed. This suggests a mixture state with chromium oxide and metallic chromium. However, chromium becomes metallic at >5 MLE coverage. From the XPS results, the behaviour of chromium on the V$_2$O$_3$(0001) surface is very similar to that of vanadium on the Cr$_2$O$_3$(0001) surface.

Similar to the case of vanadium deposited on the Cr$_2$O$_3$(0001) surface, the BE of O 1s remains unchanged with increasing chromium deposition and the obvious peak attributed to O 1s at chromium coverage of 12 MLE can still be seen in figure 5, but no line attributed to V 2p appears in the corresponding XP spectrum at the same chromium coverage, as shown in figure 5. This is also due to the residual oxygen in the chamber, which resembles the case of vanadium deposited on the Cr$_2$O$_3$(0001) surface.

The reduction of V^{3+} cations is also observed at initial coverage. As seen in figure 5, a shoulder at 513.5 eV appears and it becomes more obvious with increasing chromium deposition (from top to bottom in figure 5). From the BE, this should be attributed to V^{2+} cations and metallic vanadium. Thus, it indicates that V^{3+} can be reduced to V^{2+} and metallic vanadium by chromium at the interface of Cr/V$_2$O$_3$(0001), and different kinds of chromium cation form at the same time.
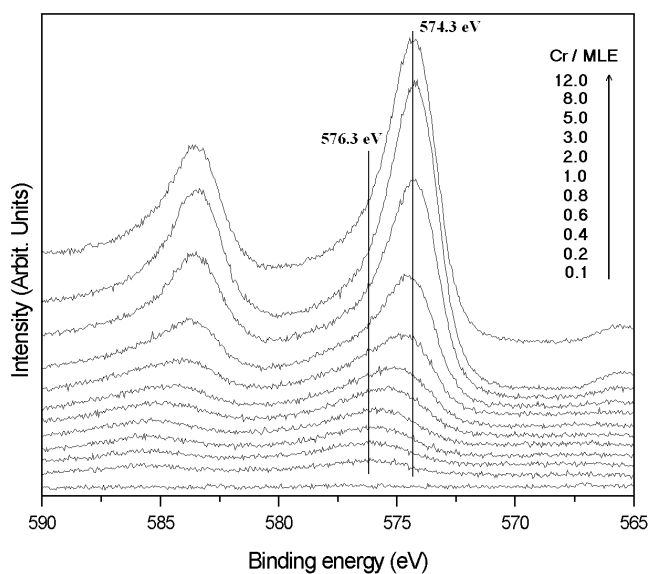
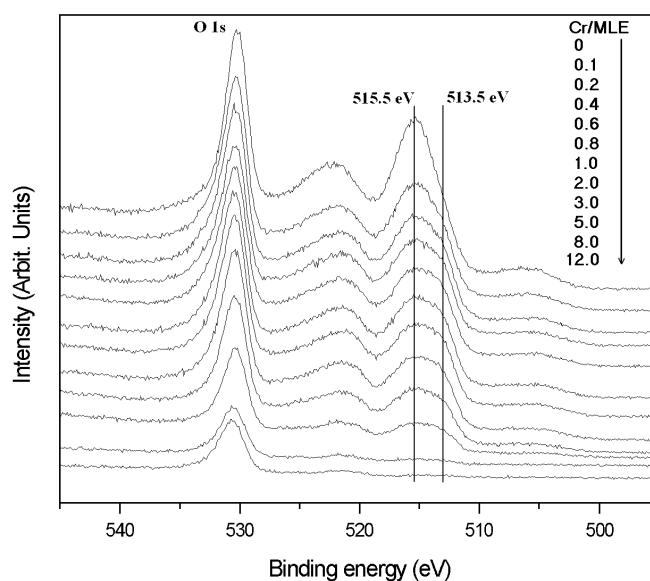**Figure 4.** XPS of Cr 2p as a function of chromium coverage.

Figure 5. XPS of V 2p and O 1s as a function of chromium coverage.

No LEED pattern is observed at chromium coverage greater than 0.4 MLE on the $V_2O_3(0001)$ surface, showing that the deposited chromium is disordered.

3.4. Oxidation of chromium on $V_2O_3(0001)$ film

The oxidation of the chromium overlayer on the $V_2O_3(0001)$ surface has also been studied using XPS. After exposure to O_2 at 1×10^{-7} mbar for 10 min at RT, the peak at 576.3 eV BE is obvious besides a peak at 574.3 eV (see figure 6(b)). This is an indication that part
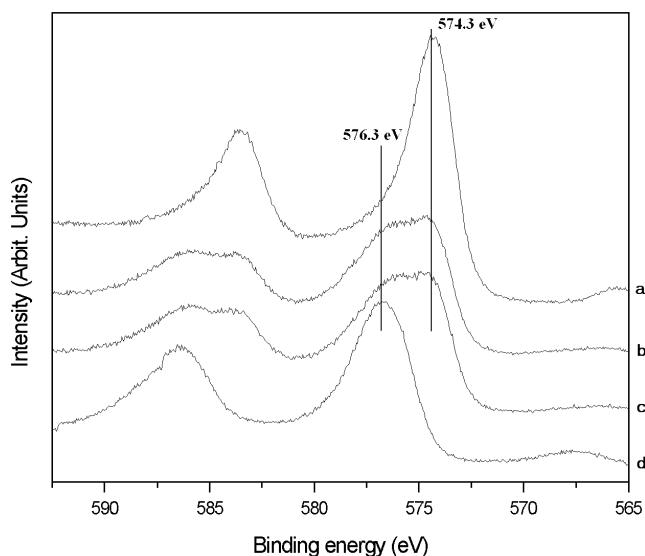
Figure 6. XPS of Cr 2p in different oxidizing conditions. (a) Metallic vanadium with a thickness of 12 MLE; (b) after exposure to oxygen at RT for 10 min (1×10^{-7} mbar O$_2$); (c) after exposure to oxygen at RT for 20 min (1×10^{-7} mbar O$_2$); (d) after exposure to oxygen at 600–700 K for 5 min (1×10^{-7} mbar O$_2$).

of the chromium has been oxidized. Similar to that of the V/Cr$_2$O$_3$(0001) system, further O$_2$ exposure for 20 min cannot fully oxidize the chromium at RT, since a peak at 574.3 eV can still be observed (see figure 6(c)). However, the surface can be fully oxidized under O$_2$ exposure combined with sample heating at 600–700 K for 5 min, as shown in figure 6(d). After annealing the sample in oxygen ambient several times, a hexagonal LEED pattern can be observed (not shown here). Since no V signal can be detected by XPS, it appears that an ordered binary oxide film of Cr$_2$O$_3$(0001) on V$_2$O$_3$(0001) is formed on the Re(0001) surface.

3.5. General remarks

In this work, the oxidation of chromium on V$_2$O$_3$(0001) and vanadium on Cr$_2$O$_3$(0001) are observed. One may argue that the shift of BE is attributable to the size effect. It is true that the small particles cause an energy shift to the higher-BE side, but no reduction of the oxide substrates should be observed. Thus our results lead to the conclusion that strong interaction exists at the interfaces of chromium/V$_2$O$_3$(0001) and vanadium/Cr$_2$O$_3$(0001). Charge transfer from the deposited metal overlayer to the oxide substrate is assumed.

In our previous studies of copper on V$_2$O$_3$(0001) and Cr$_2$O$_3$(0001) surfaces, even though Cu$^+$ cations are observed at submonolayer coverage, no obvious signal of reduced V^{3+} or Cr^{3+} is observed [3, 4]. This implies that the interaction between Cu and the V$_2$O$_3$(0001) or Cr$_2$O$_3$(0001) surface is weaker than that of Cr on V$_2$O$_3$(0001) or V on Cr$_2$O$_3$(0001) films. Bender *et al* [13] reported the formation of magnesium oxide and chromium metal when magnesium was deposited on the Cr$_2$O$_3$(0001) surface, suggesting stronger interaction between magnesium and Cr$_2$O$_3$(0001) compared with that of V on Cr$_2$O$_3$(0001). These reveal that the oxygen affinities of Cu, V and Mg increase in the order of Cu < V < Mg. However, for Cr and V, we cannot distinguish which one has higher oxygen affinity from our experiments alone. This is very reasonable since both vanadium and chromium have several oxidation states and

their low-oxidation states are stable in vacuum. The heats of formation of Cu_2O, Cr_2O_3, V_2O_3 and MgO are 170.7, 378.2, 406.3 and 601.2 kJ (mol O)$^{-1}$, respectively[2], which coincides with our experiments and discussions. The results for different metals deposited on $TiO_2(110)$ and $Al_2O_3(0001)$ surfaces are also consistent with our argument [14, 15].

Because both Cr_2O_3 and V_2O_3 have corundum crystal structures with small lattice constant mismatch, it is favourable to form an ordered $V_2O_3(0001)$ overlayer on the $Cr_2O_3(0001)$ surface and vice versa, as we have observed by LEED. For example, ordered binary oxide films of $V_2O_3(0001)/Al_2O_3(0001)$ on Mo(110) have been successfully synthesized [7].

4. Conclusions

We have studied the interfacial reaction of $V/Cr_2O_3(0001)$ and $Cr/V_2O_3(0001)$ systems by XPS and LEED. The results show that at submonolayer coverage of V the vanadium oxide forms whereas the $Cr_2O_3(0001)$ surface is reduced due to the interaction of vanadium with the Cr_2O_3 surface; vanadium becomes metallic at coverage greater than 5 MLE. Thorough oxidization of the deposited vanadium cannot be achieved by O_2 exposure at RT for 20 min, whereas a binary film of $V_2O_3(0001)/Cr_2O_3(0001)$ has been observed after heating the sample to 600–700 K in O_2 ambient at 1×10^{-7} mbar for 5 min. For the system of chromium on $V_2O_3(0001)$, similar results have been obtained.

Acknowledgments

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