Segregation of K and its effects on the growth, decoration, and adsorption properties of Rh nanoparticles on TiO$_2$(1 1 0)

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ABSTRACT

In order to understand the promoting mechanism of alkali additives, we have studied potassium overlayers on TiO$_2$(1 1 0). The surface was prepared by thermal segregation of K from the bulk to the surface above 750–800 K. The bulk diffusion of the Ti/O ions is required for the migration of large K ions inside the lattice. STM and LEIS revealed that segregated potassium forms small clusters of 1–2 nm on the surface, containing also oxygen. These clusters are located preferentially on the one-dimensional defect sites (Ti$_2$O$_3$ strings) of the (1 × 1) rutile surface and on the Ti$_2$O$_3$ rows of the (1 × n) reconstructed surfaces. According to XPS, the potassium on the surface after segregation at 1000 K is only partially ionized and the Ti 2p region is dominated by the Ti^{4+} component. XPS and LEIS provided evidence of a very clear preference for the Rh clusters to grow near 300 K *not* on the potassium structures but on the potassium-free parts of titania surface. This finding may imply the absence of a direct contact between Rh and K at low Rh coverages. Nevertheless, evaporation of Rh on K/TiO$_2$(1 1 0) results in more cationic K sites, due to an electron transfer from K to Rh through titania. The decoration and encapsulation of Rh nanoparticles by TiO$_x$ proceed also in the presence of potassium. The capping layer does not contain potassium. At large Rh cluster sizes, the wheel-like structure of the cover layer could be identified with a structure found on top of Rh crystallites formed on the K-free titania surface. The presence of potassium stabilized CO on Rh nanoparticles, which is attributed to the indirect charge transfer from potassium structures to rhodium (long range effect).

1. Introduction

Alkali additives are extensively applied as promoters in heterogeneous catalysis, like in ammonia synthesis, ethylene epoxidation, Fischer–Tropsch synthesis (FTS), alcohol synthesis, water–gas shift reaction (WGS), and also in gas sensors [1–3]. In order to shed light on the mechanism of alkali promotion, the interaction of alkali atoms with well-defined metal single crystal surfaces, and the adsorption and reactions of various compounds on alkali covered surfaces were thoroughly investigated [4–9]. In order to mimic more accurately the morphology of real catalysts, to bridge the so-called "material gap", two-dimensional model catalysts can be prepared depositing metals on single crystalline oxide surfaces, and the structure and reactivity can be revealed by the wide arsenal of surface science both at low and high pressures [10–16]. Accordingly, an increasing number of studies has been reported on the interaction of alkali with oxide surfaces [10–12], but in surprisingly

few cases also in the presence of a catalytically active metal [17,18]. In a previous study of ours, we have shown that surface potassium significantly affects the morphology (average size and distribution) of Au nanoparticles on TiO$_2$(1 1 0) [17].

In the model experiments related to alkali promotion, the deposition of alkali metals characteristically resulted in a substantial decrease in the work function both on metal and on oxide single crystal surfaces, and also in some band bending for oxides [4–10]. The bonding with titania is highly cationic at small alkali coverages ($\Theta_K \sim 1/4$–$1/2$ ML, where 1 ML is defined as one alkali site per surface unit cell of titania), due to an electron transfer from the alkali atom to TiO$_2$, while depolarization occurs approaching $\Theta_K = 1$ ML due to the repulsive interactions among neighboring dipoles. Accordingly, a dramatic broadening of thermal desorption features toward lower temperatures was experienced at higher alkali coverages (still below 1 ML) [10]. These characteristics are similar to what was found for alkali adsorption on metal surfaces [4,5].

As regards the binding sites, surface extended X-ray fine structure (SEXAFS) analysis indicated that potassium atoms/ions are bonded to oxygen sites with an inclined bridge or threefold hollow geometry on rutile TiO$_2$(1 0 0) and TiO$_2$(1 1 0) surfaces [19,20]. Inter-

estingly, according to scanning tunneling microscopy (STM) and atomic force microscopy (AFM) studies, the repulsive interaction among neighboring K ions cannot prevent the formation of K covered islands, or one-dimensional condensed structures [17,20,21]. It suggests that the electronic and structural effects combine strongly and it should be taken into account during the interpretation of any special phenomenon related to alkali additives.

Unlike on metal surfaces, alkali metal adsorption on oxides may result in a redox reaction leading to the reduction of the substrate, as was observed for K on $Fe_3O_4(1 1 1)$ [22], K on NiO(1 0 0) [10], Na on $TiO_2(1 1 0)$ [11], and for many other systems. In photoemission studies, the appearance of reduced Ti^{3+} (and even Ti^{2+}) sites was detected due to K deposition on titania, as well as the occupation of Ti 3d states in the band gap of TiO_2 [19,23]. According to calculations, the transferred charge is delocalized among the adjacent Ti ions [24,25]. Photoemission results related to the thermal behavior showed that the surface concentration of reduced Ti sites almost disappeared after high temperature annealing (1020 K), even when the coverage was still as high as $\Theta_K = 0.5$ ML [25,26].

In contrary to most model experiments, where alkali *atoms* were evaporated onto the sample, during the preparation of realistic polycrystalline catalysts, the alkali component is added to the slurry in the form of *ionic* compounds. Of course, in that way, the reduction of the support oxide, which certainly influences its reactivity, does not necessarily proceed. The potassium overlayer is prepared in this study not by evaporation, but by thermal segregation of potassium from rutile $TiO_2(1 1 0)$ crystals. Note that potassium contamination is very probably of ionic nature within the bulk of titania crystals.

The segregation of K from titania was investigated only in one previous study, using a $TiO_2(1 0 0)$ crystal [27]. The accumulation of potassium in the outermost atomic layer of the surface was observed at 675 K and above. At 975 K, however, no potassium was detected on the topmost atomic layer, but was still present in the sampling depth of Auger electron spectroscopy (AES). The segregation of Ca to $TiO_2(1 1 0)$ produces a rather smooth, well-ordered overlayer [28], indicating that Ca remains in intimate contact with the substrate. Based on calculations, a significantly relaxed, complex surface structure was proposed, which was not assigned to bulk like CaO or to any of the bulk calcium titanates [28].

For the understanding of alkali promotion, it is a key issue to disclose, whether the alkali additive is located on the metal or on the support, and to identify its chemical nature. Accordingly, we investigated the nucleation and growth of Rh on a potassium-covered $TiO_2(1 1 0)$. Beside structural properties, charge transfer processes are also of outmost importance in catalytic promotion. The results related to this latter aspect are presented as well.

It is well established that due to reduction in H_2 atmosphere, a TiO_x capping layer is formed on Ni, Pd, Rh, Ir, and Pt clusters supported by TiO_2, which is a key factor in the so-called Strong Metal Support Interaction (SMSI) [12,29,30]. The encapsulation of the clusters of these metals by TiO_x proceeds in vacuum even in the absence of H_2, if the TiO_2 sample is sufficiently reduced [31–34]. It is an important question, how the presence of an alkali influences this process. In the previous studies related to high surface area powder materials, it was assumed that the presence of potassium significantly facilitates the decoration process through the formation of potassium hydroxides and titanates [35]. This point is analyzed also in the present paper.

2. Experimental

The experiments were carried out in two different UHV systems evacuated down to 5×10^{-8} Pa.

1. The first one (denoted as the XPS-LEIS chamber) was equipped with a hemispherical analyzer (Leybold EA10/100) for performing low-energy ion scattering (LEIS), X-ray photoelectron spectroscopy (XPS), and AES measurements. A quadrupole mass spectrometer was also built in for thermal desorption spectroscopy (TDS). For LEIS, He ions of 760 eV kinetic energy were applied (0.03 $\mu A/cm^2$), while the scattering angle was 95°. Note that LEIS supplies information almost exclusively about the outermost atomic layer, when performed with noble gas ions. An Al Kα X-ray source was applied for XPS. The binding energy scale was referenced to the $4f_{7/2}$ peak of a thick Au layer, fixed at 83.8 eV. The pass energy was typically 100 eV, but for the Auger parameter analysis 10 eV. If not mentioned otherwise, the take-off angle (θ) was 16°, with respect to surface normal. The X-ray satellites at 9.8 and 11.8 eV away from the main lines were removed in the Ti 2p, K 2p, and Rh 3d regions by subtracting the given spectrum after scaling and x-shifting, taking into account that the respective intensities are 6.4% and 3.2% of the main intensities [36]. For the O 1s region, this procedure was not necessary, because the influence of X-ray satellites on the peaks was negligible. CO (99.97% purity) was dosed through a capillary. During TDS measurements, the sample was in line of sight and the heating rate was 1 K s^{-1}.

2. In the second UHV chamber (denoted as the STM chamber), a commercial room temperature STM (WA-Technology) and a cylindrical mirror analyzer with a central electron gun (Staib-DESA-100) for AES were built in. For STM imaging, chemically edged IrPt or W tips were applied and sharpened "in situ" over the TiO_2 surface by using 5–10 V pulses. Typical tunneling parameter of +3 V (0.1 nA) was applied due to the relatively high band gap of the overlayer. In the case of clean surface, the imaging bias of +1.5 V proved to be sufficient.

In both chambers, rutile $TiO_2(1 1 0)$ single crystals of the same manufacturer were applied, and the probe temperature was measured by a chromel–alumel (K-type) thermocouple stuck to the side of the samples by a UHV compatible oxide adhesive (Ceramobond 569, Aremco). The probes were resistively heated (1–2 K s^{-1}) with a Ta filament. The samples were routinely cleaned applying Ar$^+$ ion sputtering (10 μA cm^{-2}, 1.5 keV, 10 min, 300 K) and vacuum annealing (10 min, 1000–1050 K) cycles. After a short annealing at 1050 K in UHV, the surface of the $TiO_2(1 1 0)$ probe obtained in this way exhibited mainly (1 × 1) ordered phase accompanied by some (3–5% of the total surface area) protruding dots and 1D stripes in the [0 0 1] orientation [37].

The potassium overlayer in this work was prepared by thermal segregation. Generally, the potassium content of a TiO_2 crystal is exhausted by 30–50 sputtering–annealing cycles. This was the case for the samples studied in the STM chamber, and for this reason, several samples had to be used to perform the experiments. On the other hand, for the sample investigated in the XPS-LEIS chamber, the K coverage obtained by 5–10 min annealing at 1000 K was stable during the period of the experiments (~3 month), characterized by a K/Ti AES ratio of $R_K = 0.9$, obtained from the peak-to-peak intensities of the main K_{LMM} (252 eV) and Ti_{LMM} (385 eV) peaks in the differential mode. Other typical impurities (Ca, Mg, Na) were not present in the samples. The coverage of potassium is defined in this work as the number of surface potassium atoms/ions per unit cell area of the unreconstructed $TiO_2(1 1 0)$ surface (1 ML ∼ 5.20×10^{14} cm^{-2}). In the STM chamber, potassium coverage was determined from R_K ratios [21]. In the XPS-LEIS chamber, K coverage was determined from XPS peak areas applying photoelectric cross-sections and inelastic-mean-free-path (imfp) values of Scofield [38] and Seah and Dench [39]. At $R_K = 0.9$, the potassium coverage calculated this way was 0.9 ML. It was assumed that the same R_K AES ratios in the different chambers corresponded to comparable coverages, using Auger spectra collected with the same primary energy (3 keV) and with constant pass energy in both systems.