Oxidation State and Size Effects in CoO Nanoparticles

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We have investigated the oxidation state and size effects on the electronic structure of 10 and 20 nm CoO nanoparticles by means of surface spectroscopies. It has been concluded that the surface of the as-grown CoO nanoparticles is oxidized to Co_3O_4. After annealing of the nanoparticles in UHV at 600 °C, the surface is reduced to CoO. The results show that the electronic structure of the as-grown 20 nm CoO nanoparticles is not significantly affected by surface effects and compares rather well with a CoO bulk sample. However, in the case of the 10 nm CoO nanoparticles, size effects are clearly observable since the relatively large surface-to-volume ratio of these nanoparticles produces a large amount of surface defects which act as adsorption centers.

Introduction

The main purpose of this work is to study the oxidation state and size effects in CoO nanoparticles of two different particle size. It is known that materials grown as particles in the nanometer scale show unique chemical and physical properties. For instance, size effects play an important role in catalysis. However, many questions concerning the properties of nanoparticles remain still open. In particular, the critical size at which these properties are modified with respect to those of bulk materials is an important question that is not well understood yet. This work is focused on a comparative analysis of CoO nanoparticles of 10 and 20 nm. The nanoparticles were analyzed by means of X-ray photoelectron (XPS) and X-ray absorption (XAS) spectroscopies. It is shown below that these techniques provide valuable information on the oxidation state of the nanoparticles. In addition, surface effects were studied with the more surface sensitive photoemission spectroscopy (PES) using synchrotron radiation tuned at $h\nu = 170$ eV photon energy. We show below that adsorption is clearly enhanced in the case of the smaller nanoparticles (10 nm). These size effects are attributed to surface defects, which act as adsorption centers.

The unique catalytic and magnetic properties of highly defective transition metal nanoparticles were first reported by Gravelle et al.[1] Since then, considerable attention has been paid to the study of the electronic structure of this kind of particles, mainly NiO.[2−6] Early XPS studies on NiO nanoparticles showed the appearance of satellite structures in the O 1s and Ni 2p XPS spectra that were first attributed to the presence of Ni^{3+} ions.[3,4] However, a posterior characterization by X-ray absorption spectroscopy (XAS) showed that Ni ions in NiO nanoparticles

(2−5 nm) are unambiguously present in the high-spin Ni^{2+} form.[5] Furthermore, the complex O 1s XAS spectra were interpreted as being due to a distortion of the crystal field induced by the large surface-to-volume ratio and the high concentration of surface defects.[5] These defects were attributed to unsaturated NiO bonds which act as adsorption centers.[6]

The XPS analysis of these CoO nanoparticles has been reported previously.[7] In that work, it was found that the surface composition and electronic structure of the particles approached that of Co_3O_4. A posterior annealing of the nanoparticles led to the reduction to CoO. In addition, it was found that the O 1s XPS peak was formed by a main line and a small satellite separated by 1 eV at higher binding energy. This satellite was attributed to surface defects which depended on the texture of the sample, i.e., on the particle size.[7] Other works dealing with the preparation of CoO nanocrystals have been reported recently.[8] Many other works involving the study of cobalt oxides using spectroscopic techniques, mainly XPS, have also been reported[9−14]

Experimental Section

Samples of CoO nanoparticles with two different particle sizes were used in this work. The first sample was a commercial powder obtained from Merck with an averaged particle size of 20 nm. The second sample, prepared in our laboratory following the method described by Gravelle et al.,[1] gave particles with an average size of about 10 nm. The average particle size was determined by using transmission electron microscopy (TEM). The samples were also characterized by X-ray diffraction (XRD), showing the characteristic rock-salt structure, as expected for CoO. The effective surface area was measured using the BET method, being 30 m^2 g^{-1} for the 20 nm particles and 60 m^2 g^{-1} for the 10 nm particles. More details on the preparation and characterization of the samples can be found elsewhere.[1,7]

The XPS spectra were taken in a VG-Escalab 210 spectrometer at 50 eV pass energy using a Mg Kα radiation source and

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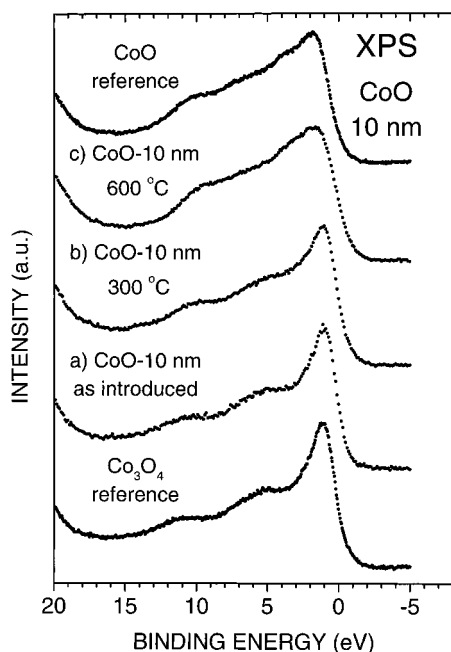*J. Phys. Chem. B, Vol. 103, No. 32, 1999* **6677**

Figure 1. Valence band XPS spectra of the Co_3O_4 reference sample; 10 nm CoO nanoparticles (a) as introduced, (b) after annealing in UHV at 300 °C, and (c) after annealing in UHV at 600 °C; and the CoO reference sample.

Figure 2. Valence band XPS spectra of the Co_3O_4 reference sample; 20 nm CoO nanoparticles (a) as introduced, (b) after annealing in UHV at 300 °C, and (c) after annealing in UHV at 600 °C; and the CoO reference sample.

giving an overall resolution of 1.0 eV. The XAS and PES spectra were measured at the SU7 beam-line in the Super Aco storage ring at LURE (Orsay) by using a TGM-10m monochromator. The photon energy used in the photoemission measurements was set at 170 eV, giving a total resolution of about 300 meV. The O 1s XAS spectra were recorded in the total electron yield detection mode. The estimated resolution at this edge was better than 800 meV. The XAS spectra were normalized to the incident photon intensity to correct from possible variations of the beam.

Results and Discussion

a. Oxidation State of the Nanoparticles. In this section, we are going to investigate the oxidation state of the Co atoms at the surface of the CoO nanoparticles by means of XPS and XAS. To this end, we have measured the valence band XPS and the O 1s XAS spectra of the nanoparticles as introduced in the UHV chamber and after different annealings up to 600 °C. Then, the spectra are compared to those of CoO and Co_3O_4 reference bulk samples.

The valence band XPS spectra of the 10 and 20 nm CoO nanoparticles as introduced and after annealing in UHV at different temperatures are shown in Figures 1 and 2, respectively. In both figures, the spectra of the nanoparticles are compared to those of CoO (top) and Co_3O_4 (bottom) reference samples. The reference spectra are in very good agreement with previous reports[14] for the same compounds. In fact, the nature of these spectra has already been extensively discussed in the literature.[14,15] The spectrum corresponding to CoO (Co^{2+}) coincides with the spectral weight of a CoO_6 cluster calculation when a Co 3d electron has been removed, as shown in ref 14. The spectrum of Co_3O_4 is between those corresponding to CoO (Co^{2+}) and to $LiCoO_2$ (Co^{3+}), according to the respective positions (i.e., two octahedral and one tetrahedral) of the Co ions in Co_3O_4.[14]

First of all, we point out the similarity of the spectra for both sizes of CoO nanoparticles (cf. Figures 1 and 2). This indicates that, although the history of the nanoparticles is different, i.e.,
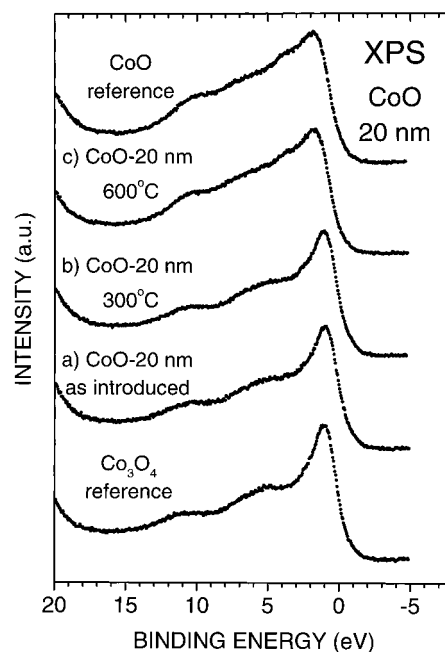
they have been prepared by different methods, the valence band XPS spectra show exactly the same electronic structure. For both particle sizes, the valence band spectra of the as-introduced CoO nanoparticles (Figures 1a and 2a) reproduce very closely that of the Co_3O_4 reference sample. The spectra taken after annealing at 300 °C (Figures 1b and 2b) do not change significantly with respect to the previous ones. However, the spectra taken after annealing at 600 °C (Figures 1c and 2c) exhibit significant changes and now resemble that of the CoO reference sample.

Similar results are obtained by XAS. The O 1s XAS spectra of the 10 and 20 nm CoO nanoparticles as introduced and after annealing in UHV at different temperatures are shown in Figures 3 and 4. The O 1s XAS spectra of the nanoparticles are also compared to the same spectra of the CoO and Co_3O_4 reference samples. These reference spectra are in very good agreement with previous reports in the literature.[14] In general, the O 1s XAS spectra reflect the partial density of O p unoccupied electronic states in the conduction band.[16] In particular, the region between 530 and 535 eV corresponds to transitions to unoccupied electronic states of O p character hybridized with Co d states. The region above 535 eV is mainly due to transitions to O p states hybridized with states of Co 4s,4p character. [17]

Once again, we note the close resemblance between the spectra of the two different particle sizes (cf. Figures 3 and 4). As in the case of the XPS spectra, the O 1s XAS spectra of the as-introduced CoO nanoparticles (Figures 3a and 4a) reproduce very well that of the Co_3O_4 reference sample. The spectra taken after annealing at 300 °C (Figures 3b and 4b) do not change with respect the previous ones, whereas the spectra taken after annealing at 600 °C (Figure 3c and 4c) resemble again the spectrum of the CoO reference sample.

Three important conclusions can be inferred from the data presented in this section. First, the electronic structure of the nanoparticles of 10 and 20 nm particle size are rather similar as observed by XPS and XAS. This is important since the two different kinds of nanoparticles have been grown using different methods. Second, whereas XRD analysis[7] reveals that the
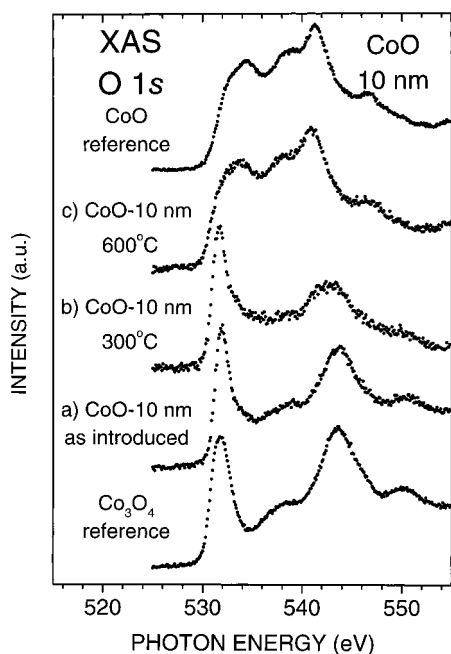
Figure 3. O 1s XAS spectra of the Co_3O_4 reference sample; 10 nm CoO nanoparticles (a) as introduced, (b) after annealing in UHV at 300 °C, and (c) after annealing in UHV at 600 °C; and the CoO reference sample.

Figure 4. O 1s XAS spectra of Co_3O_4 reference sample; 20 nm CoO nanoparticles (a) as introduced, (b) after annealing in UHV at 300 °C, and (c) after annealing in UHV at 600 °C; and the CoO reference sample.

volume of the nanoparticles corresponds to Co^{2+}, their surface become oxidized to Co_3O_4 when exposed to the atmosphere. The surface of the as introduced nanoparticles is oxidized to a depth of, at least, the mean probing depth of XPS and XAS (about 2 and 4 nm,[18] respectively). And third, the surface of the CoO nanoparticles is reduced back to CoO after annealing in UHV at temperatures between 300 and 600 °C. These conclusions are in perfect agreement with those obtained from the analysis of XPS core-level spectra.[7]

b. Size Effects in 10 nm CoO Nanoparticles. To investigate the surface region of the nanoparticles in more detail, we have also measured the valence band photoemission spectra (PES) with $hv = 170$ eV. At this photon energy, the PES spectra are much more surface sensitive with a mean probing depth of less than 1 nm. In addition, at this photon energy, the photoemission cross section of the O 2p is at least 100 times larger than that for XPS.[19] This means that the PES spectra are more sensitive to surface adsorbates than those of XPS and XAS.

The valence band PES spectra of the 10 and 20 nm CoO nanoparticles as introduced are shown in Figure 5. These spectra are compared with the spectrum of the Co_3O_4 reference sample (Figure 5c). The spectrum of the as-introduced 20 nm CoO nanoparticles (Figure 5b) reproduces very closely that of the Co_3O_4 reference sample. They present also similarities with the XPS valence band spectra depicted in Figures 1 and 2. In fact, they show the same structures in the valence band. The differences are mainly due to the different values of the photoemission cross section of the valence states for XPS and PES and to the better resolution obtained with synchrotron radiation.

The close resemblance of the spectra corresponding to the 20 nm CoO nanoparticles with the reference bulk materials suggests that surface effects do not play a major role for *this particle size* (20 nm). In contrast, the spectrum of the as-introduced 10 nm CoO nanoparticles (Figure 5a) presents significant differences with respect to that of the bigger particles. The main differences are the appearance of a strong bump at a
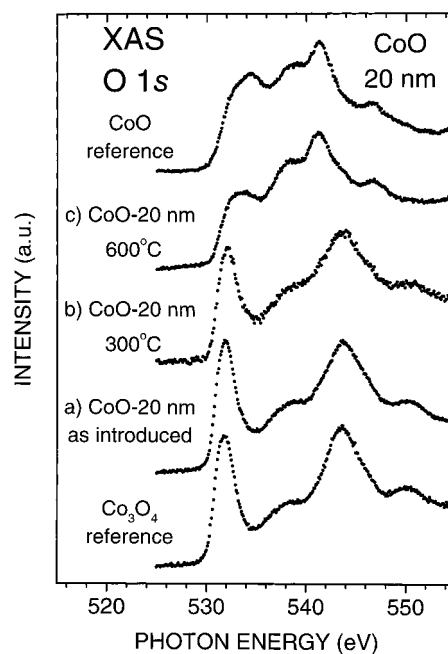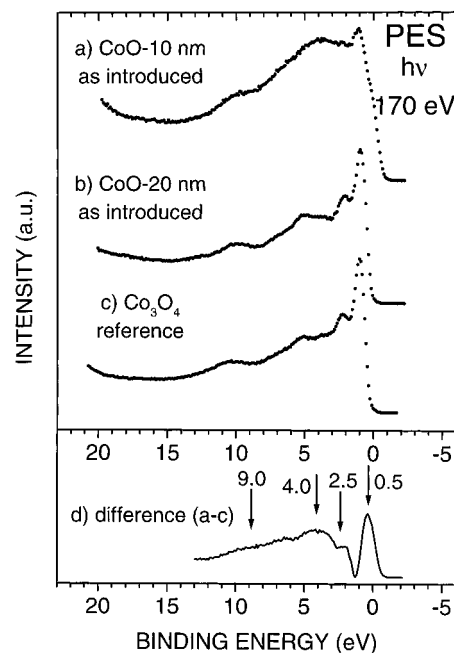

Figure 5. Valence band PES spectra ($hv = 170$ eV) of CoO nanoparticles as introduced in UHV (a) 10 nm and (b) 20 nm, (c) Co_3O_4 reference sample, and (d) difference spectrum (a − c).

binding energy of around 4 eV and a shoulder at the Fermi level. To clarify the origin of such structures, we have performed the subtraction of the reference spectrum associated with Co_3O_4 from the spectrum corresponding to the 10 nm nanoparticles as introduced. The difference spectrum is labeled as Figure 5d and indicates rather clearly an enhancement of the photoemission signal in the 2−10 eV binding energy range with three structures at ca. 2.5, 4, and 9 eV as well as a sharp peak at about 0.5 eV below the Fermi level. The relative intensity and energy position of the three structures observed in the region between 2 and 10 eV have been previously observed by Jeng et al.[12] when a defective Ar-bombarded CoO single crystal was exposed to
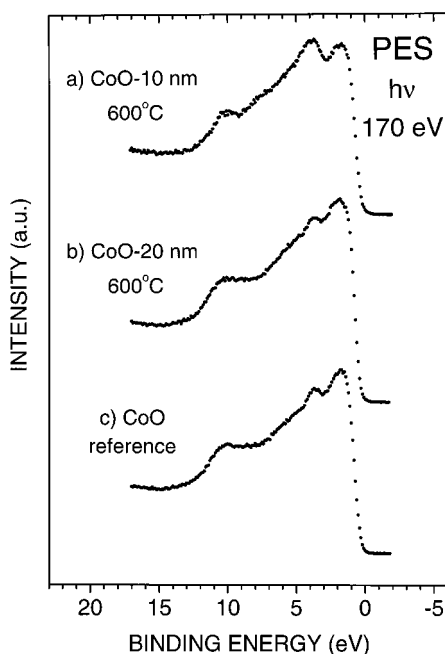
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Figure 6. Valence band PES spectra (*hν* = 170 eV) of CoO nanoparticles after annealing in UHV at 600 °C (a) 10 nm and (b) 20 nm and (c) CoO reference sample.

oxygen. According to this, we attribute this bump to adsorbed oxygen species.

These results clearly indicate that, whereas the surface of the 20 nm CoO nanoparticles resembles that of Co_3O_4, the spectrum associated to the small nanoparticles seems to be highly influenced by a larger adsorption of oxygen species. This is consistent with the existence of a higher concentration of point defects at the surface of the 10 nm nanoparticles, induced by the relatively larger surface-to-volume ratio for this particle size, which acts as adsorption centers. We want to recall here similar results obtained for 2−5 nm NiO nanoparticles grown by the same method.[6]

The sharp peak at the Fermi level in the difference spectrum arises from the shoulder observed at the Fermi level in the spectrum of the 10 nm CoO nanoparticles, which is not present in the spectrum of the 20 nm nanoparticles. Obviously, it is not due to oxygen species, since the binding energy is too low. At these binding energies, only Co 3d states are expected to contribute to the photoemission signal.[12,14] According to that, this feature is attributed to a splitting of the Co 3d states due to the presence of point defects, i.e., a distortion of the crystal field, in agreement with the interpretation given to similar results for NiO nanoparticles.[6]

The valence band PES spectra of the 10 and 20 nm CoO nanoparticles taken after annealing in UHV at 600 °C are shown in parts a and b of Figure 6. These spectra are compared here with the reference spectrum for CoO (Figure 6c). In this case, the spectra of the two types of nanoparticles approach the reference spectrum for CoO. This clearly indicates that after annealing both surfaces reduce from Co_3O_4 to CoO. However,

the spectrum of the 10 nm nanoparticles still presents a small bump around 4 eV, suggesting that the healing of defects is not completed.

Conclusions

In summary, the results presented here show that the surface of the as-introduced CoO nanoparticles appears oxidized up to Co_3O_4, although annealing in UHV at 600 °C reduces the surface of the nanoparticles to the nominal CoO composition. Surface effects do not significantly affect the electronic structure of the 20 nm CoO nanoparticles. However, in the case of the 10 nm CoO nanoparticles, surface effects are observed as a large amount of point defects which adsorb mainly oxygen species. Although the data presented here show clear differences in the surface chemistry between the smaller (10 nm) and the bigger (20 nm) CoO nanoparticles, which have been attributed to size effects, more work involving a wider size range (i.e., 3−15 nm) of nanoparticles would be desirable in order to estimate the critical size at which these effects play an important role.

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