Valence and Coordination State of Cobalt Atoms in Bulk and Deposited Lanthanum Cobaltates

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Received December 14, 2005

Abstract—The valence and coordination state of paramagnetic cobalt atoms in bulk phases of perovskite cobaltate $LaCoO_3$ and cobalt oxide Co_3O_4 and in nanosized $LaCoO_3$ deposited inside the mesoporous molecular sieve MCM-41 matrix has been studied using ESR. Cobalt(II) cations in deposited cobaltates have octahedral coordination, which is characteristic of perovskite-like structures.

Electron spin resonance provides detailed information not only on the valence and coordination state of paramagnetic transition-metal ions in oxide materials but also on their local symmetry. Perovskite cobaltates of the general formula $LnCoO_3$ (where Ln stands for a lanthanide) are very interesting in this respect. In ideal structures of this type, cobalt exists in the form of diamagnetic cobalt(III) ions; in real perovskite phases, however, there is always a deficit of oxygen. The generation of oxygen vacancies is accompanied by a decrease in the formal oxidation number of some structural ions: $Co(III) \longrightarrow Co(II)$; the latter retain the octahedral oxygen coordination.

The imperfection of real oxide phases to a large extent dictates the physical and physicochemical characteristics of these materials; through this, imperfection dictates their functional properties, in particular catalytic activity, which is substantially affected by the defect density. Here, we carry out an electron spin resonance (ESR) study of bulk and deposited lanthanum cobaltates ($LaCoO_3$) in order to determine their cobalt(II) paramagnetic centers. Such oxide materials attract the attention of researchers on the following accounts: they do not contain precious metals, are environmentally friendly, and are efficient catalysts for the oxidation of organics and CO.

EXPERIMENTAL

Bulk $LaCoO_3$ and Co_3O_4 phases were prepared by the thermooxidative degradation of lanthanum cobalt and cobalt citrato complexes, respectively. The citrato complexes were prepared as in work [1] in the following fashion. Lanthanum and cobalt nitrates were dis-

solved in aqueous citric acids; the resulting solution was continuously stirred for 24 h at room temperature, and then used in the synthesis.

The bulk samples were prepared as follows. A solution of the citrato complex was concentrated to a dry residue at 100°C for several hours; the residue was calcined in air at 600°C for 8 h. In this way, lanthanum cobaltate ($LaCoO_3$) and cobalt oxide (Co_3O_4) samples were obtained. Deposited cobaltate was prepared by impregnating an MCM-41 mesoporous molecular sieve (specific surface area, 860 m²/g; average pore diameter, 3.3 nm) with an aqueous solution of the citrato complex. Then, the sample was dried at 60°C and calcined in flowing air at 600°C for 8 h. A $LaCoO_3$/MCM-41 sample containing ~10 wt % cobaltate was manufactured in this way.

Powder X-ray diffraction analysis was carried out on a Dron 3M diffractometer using filtered CuK_α radiation. Electron spin resonance spectra were recorded at 295 and 77 K on an EMX Bruker spectrometer operating at ~9.3 GHz (the X band) and 100-kHz frequency modulation. The g-factor values were determined by simultaneously measuring the frequency and magnetic field. The spectra were processed using WINEPR Bruker software.

RESULTS AND DISCUSSION

The figure displays the ESR spectra for bulk Co_3O_4 (spectrum *a*) and perovskite $LaCoO_3$ (spectrum *b*); the latter nominally contains 22.1 at. % Co. Both spectra are broad asymmetric lines. The average g-factor value (g_0) corresponding to the intersection of the ESR signal with the baseline is ~2.3. The line width δH and signal intensity (double-integrated intensity) for both samples change with decreasing temperature. For $LaCoO_3$, the line width δH increases from ~1850 G at 295 K to 2350 G at 77 K; the signal intensity increases about

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threefold. Such a spectral evolution is intrinsic to paramagnetic centers. For cobalt oxide, in contrast, δH decreases with decreasing temperature, from 2100 at 295 K to 1170 G at 77 K; the increase in the signal intensity is only 1.5-fold. This result can be regarded as indicative of the existence of antiferromagnetic exchange interaction in the spin system of Co_3O_4, which is expected of cobalt oxide: Co_3O_4 contains equal numbers of low-spin diamagnetic cobalt(III) cations and paramagnetic cobalt(II) cations; the Néel temperature for Co_3O_4 is 40 K. The strong ESR signals observed in bulk Co_3O_4 and perovskite $LaCoO_3$ samples can be assigned, in accordance with works [2, 3], to paramagnetic cobalt(II) ions in different local environments involved to different extents in the exchange interaction with each other. Strong exchange interactions between cobalt(II) ions in Co_3O_4 are responsible for the resemblance of the ESR spectrum of Co_3O_4 and the previously described spectrum [2] of chain fragments

$$-Co^{2+}-O^{2-}-Co^{2+}-O^{2-}-$$
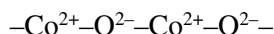
Evidently, these structural fragments cannot exist in perovskites, in which all cobalt is in the form of stable low-spin cobalt(III) ions [4]. Therefore, the appearance of the broad signal in bulk $LaCoO_3$ samples is most likely due to minor Co_3O_4 impurities, which can have been formed during the thermolysis of the citrato complex and which have not entered the composition of the cobaltate. A similar result was obtained previously in work [4]; the authors of that work studied the formation of perovskite $LaCoO_3$ during the thermolysis of a mixed citrato complex and found weak reflections from a Co_3O_4 phase in the X-ray diffraction diagram. In our case, powder X-ray diffraction does not show a Co_3O_4 phase in $LaCoO_3$; ESR, due to its high sensitivity, can detect weakly interacting cobalt(II) ions.

Apart from the strong, asymmetric ESR signal with $g_0 \sim 2.3$, a bulk $LaCoO_3$ sample exhibits two extra weak signals (spectrum b): (1) $g_0 \sim 5$ and $\delta H = 160$ G, and (2) $g_0 \sim 2$ and $\delta H = 440$ G. According to works [3–6], the signal $g_0 \sim 5$ can be assigned to isolated cobalt(II) ions. Such isolated cobalt(II) ions do not exist in the phase of the simple oxide, but they can appear as defect centers in the perovskite material, where most cobalt atoms are octahedral and have the oxidation number +3. The appearance of the ESR signals from cobalt(II) ions at 295 and 77 K implies their low-spin state ($s = 1/2$): high-spin ($s = 3/2$) cobalt(II) ions have very short relaxation times, and their ESR spectra are observable only below 20 K [4]. The weak signal with $g_0 \sim 2.0$ and $\delta H = 440$ G is likely associated either with other defect cobalt(II) centers in perovskite or with adsorption complexes of cobalt and dioxygen [7, 8].

The ESR spectrum for deposited $LaCoO_3/MCM$-41 samples (spectrum c) significantly differs from the spectrum of the bulk $LaCoO_3$ sample. The spectrum is a broad, strongly asymmetric line (at 295 K, $g_0 = 5.4$
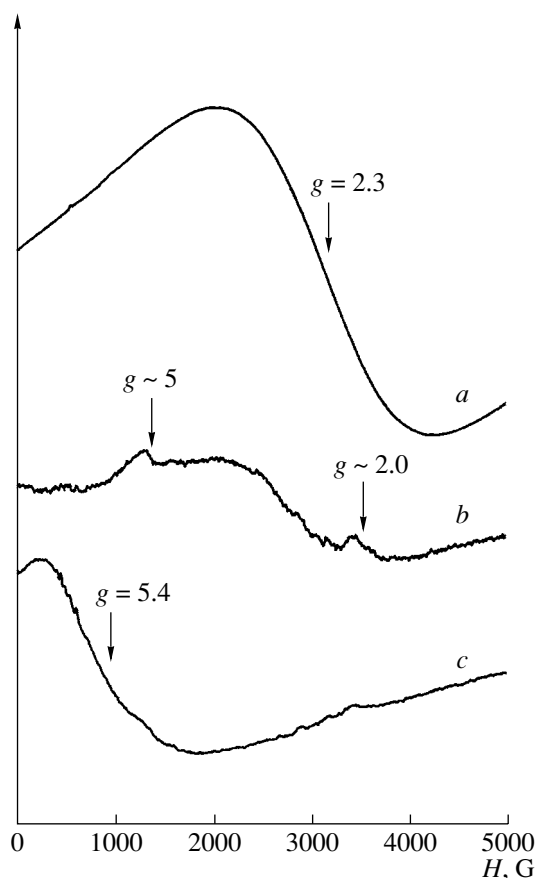
ESR spectra of (*a*) Co_3O_4, (*b*) $LaCoO_3$, and (*c*) $LaCoO_3/MCM$-41 samples at 296 K.

and $g_{max} \sim 18$). This line significantly shifts downfield compared to the spectrum of the bulk cobaltate (spectrum b). At 77 K, the signal intensity and line width appreciably increase. The g_0 value remains practically unchanged, while the downfield shift of the low-field extreme (g_{max}) becomes even greater. Analogous evolution of ESR signals was observed in work [3] from isolated cobalt(II) ions introduced by ion exchange into zeolites A and X.

By analogy with the spectrum of the bulk cobaltate sample, the ESR signal with $g_0 = 5.4$ in deposited $LaCoO_3/MCM$-41 can also be assigned to spatially separated low-spin cobalt(II) ions in octahedral coordination. Comparing the ESR spectra of bulk and deposited $LaCoO_3$, we see that in the latter, all cobalt atoms enter the cobaltate: signals with $g \sim 2.3$ from cobalt–oxygen chains, which are characteristic of Co_3O_4, do not appear in the $LaCoO_3/MCM$-41 sample. It is noteworthy that the relative intensity of the ESR signals, normalized to the overall cobalt content of the sample, in the $LaCoO_3/MCM$-41 sample is far higher than in the bulk perovskite $LaCoO_3$.

To summarize, the above data imply that nanosized cobaltate particles formed in the mesopores of the MCM-41 matrix upon the degradation of precursor

compounds, contain higher cobalt(II) concentrations than bulk lanthanum cobaltates; in the latter, cobalt(II) ions are mere defects. There are two likely reasons for this: either nanosized cobaltate particles deposited inside MCM-41 pores have a higher degree of structural nonideality than bulk perovskites, or a mixed oxide differing in composition from $LaCoO_3$ and containing cobalt(+2) is formed in MCM-41 pores.

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