ELECTRONIC, MAGNETIC AND CATALYTIC PROPERTIES OF COBALT CONTAINING SPINEL AND PEROVSKITE TYPE MATERIALS

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Abstract: Correlations between electric, magnetic and catalytic properties of various Cobalt containing spinel and perovskite type materials (e.g. Co_3O_4, $LaCoO_3$) were investigated with respect to application in environmental catalysis. As a fast test reaction the CO oxidation with air up to 400°C was chosen and found to be initiated by high-spin Co^{2+} ions at the surface. Thus, catalytic activity depends strongly on the condition of materials preparation. From comparison of the activation energies of the oxidation rate and hopping bulk charges it is concluded, that an activated charge transfer between Co^{2+} and Co^{3+} ions at the surface is the rate determining step. However, the bulk conductance itself does not play any role for catalytic activity. A hindrance for broad application of perovskite type catalysts is the fast deactivation by SO_2. As it is chemisorbed and oxidized at the active Co^{2+} sites to give sulfate, SO_2 stops the CO oxidation immediately. Only a partial recovery is possible by heating at higher temperatures, therefore the substitution of Pt metal catalysts by such materials fails, when SO_2 is present in a waste gas.

Električne, magnetne in katalitske karakteristike materialov spinelnega in perovskitnega tipa, ki vsebujejo kobalt

Izvleček: Preiskovali smo korelacije med električnimi, magnetnimi in katalitskimi karakteristikami različnih materialov, ki vsebujejo kobaltove ione in imajo spinelno ali perovskitno strukturo, na primer Co_3O_4 in $LaCoO_3$. Za hitro testiranje smo izbrali oksidacijo CO v zraku pri 400°C. Ugotovili smo, da je reakcija katalizirana s Co^{2+} ioni z visokim spinom, ki se nahajajo na površini. To pomeni, da je aktivacijska energija katalize močno odvisna od priprave materiala. Iz primerjave aktivacijskih energij hitrosti oksidacije in »hopping« prevajanja v samem materialu smo ugotovili, da je aktiviran prenos naboja med Co^{2+} in Co^{3+} ioni na površini tisti, ki določa hitrost reakcije. Prevodnost samega materiala ne vpliva na katalitsko aktivnost. Možnost široke aplikacije katalizatorjev perovskitnega tipa pa preprečuje hitra deaktivacija teh katalizatorjev z SO_2. SO_2 se adsorbira na površini in na aktivnih Co^{2+} mestih oksidira v sulfat ter tako takoj prepreči oksidacijo CO. Katalitska aktivnost se lahko samo delno obnovi s segrevanjem pri povišani temperaturi. Zato zaenkrat ni možna zamenjava katalizatorjev na osnovi platine s takimi materiali, če je v odpadnih plinih prisoten SO_2.

INTRODUCTION

Since more than two decades Co containing spinels (e.g. Co_3O_4) and perovskites (e.g. $LaCoO_3$) are well-known materials of high catalytic activity /1, 2/, for instance for gas phase oxidation with air. Further, applications in gas sensors (for CO) were taken into consideration /3,4/. Unfortunately the relevance of these materials to environmental catalysis or other purposes seems to be extremely restricted and most of the existing literature is not very promising /5-7/. When applied to real gas mixtures, there is a high risk of poisoning. On the other hand, these or similar mixed valence materials are catalytically as active as Pt or Pd and a possible substitution of the latter by oxides is still a certain commercial challenge.

The outstanding catalytic activity is supposed to be connected with a special spin or bond situation of the Co ions, which can be two, three or fourfold charged /8-13/. Most of such ideas are based on mixed-valence and crystal field models, but a direct experimental correlation or evidence for a favored high spin action has never been obtained. A similar lack of knowledge exists for a possible correlation with electric properties, which would be vital for an extended use for sensor elements.

In general spinel and perovskite type materials can be tailored in a wide stoichiometric range, behaving either insulating, semiconducting or metallic in the catalytically interesting temperature range /14-16/. So the first aim of this work was to prepare thermally stable and active materials and to investigate, whether magnetic or electric correlations with catalytic activity can be found or not. In following this way, of course, special attention had to be paid to the interpretation of results because of the basic differences of bulk and surface properties.

The second aim of this work was to investigate the applicability of spinel and perovskite type materials for the CO oxidation in waste gases with a high level of SO_2, caused by the low cost incineration of S containing fuels. To gain more basic know-how for an eventual

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application, catalytical experiments were carried out not only with powders but also with ceramic honey combs under realistic gas conditions, i.e. with reasonable space velocities /17,18/.

EXPERIMENTAL

For our investigations we chose materials, that were proved to be thermally stable in the temperature range up to 600°C. Those were:

1. Spinel type materials: $ZnNiMnO_4$, Co_3O_4.

2. Perovskite type materials: $LaCoO_3$, $LaNiO_3$, $LaNi_{1-x}Co_xO_3$, $LaAl_{1-x}Co_xO_3$, $LaTi_{1-x}Co_xO_3$, $La_{0,8}Sr_{0,2}CoO_3$.

Except Co_3O_4, which was purchased from MERCK (analytical grade), both spinel and perovskite type materials were prepared by coprecipitation of about 0,05m nitrate solutions with 3 m NaOH. After careful washing with deionised water and drying at 110°C, the calcination of hydroxides was carried out in air at different temperatures up to 1150°C for several hours. To characterize the powders the chemical stoichiometry was determined by wet chemical methods, BET surface was measured with a Quantachrome surface analyser and X-ray spectra were taken on a Siemens D5005 diffractometer. For susceptibility measurements the native powders were used of Co_3O_4, $LaCoO_3$ and $LaTi_{1-x}Co_xO_3$ at temperatures between 80K and 600K the magnetic susceptibility was measured with a modified Faraday balance. Low-temperature measure-ments between 4,2 and 80 K were performed with a Lake Shore 7121 magnetometer using liquid Helium for cooling. $KCr(SO_4)_2.12H_2O$ was used for calibration in both cases.

For electrical measurements the powders were pressed into pellets and sintered taking into account the range of stability. The DC bridge consisted of a Wenking Galvanostat LT-78 and a Knick Voltmeter. Catalytical measurements of the CO oxidation were usually made with spherical agglomerates of 0,1 to 1μm particles, sieved into a fraction of 0,5 to 1,25 mm, in an electrically heated double-tube reactor made of Pyrex glass with a inner diameter of 2 cm. The gas flow was kept constant by means of two Brooks mass flow meters 5858 TR at a space velocity of about 50 000 h^{-1}. Most experiments were carried out with a mixture of air (H_2O content <0,5vol%) and CO (0,1-1vol%). In some cases instead of air a water free mixture of 2% O_2 and 98% N_2 was used. The influence of SO_2 was studied by adding 0,1% SO_2 to the normal gas stream. The conversion of CO into CO_2 was continuously monitored by means of a CO/CO_2 IR detector Ultramat 22P from Siemens, varying the temperature stepwise. The reactor was usually filled with 2-5 g material equivalent to a height of about 1-3 cm.

Additionally small honey combs (2,5x2,5x10 cm with 25 channels) were prepared from powder mixtures of TiO_2/WO_3 (10%wt)/$LaCoO_3$ (20%wt) and SiO_2(90 %wt) /$LaCoO_3$(10 %wt) by extrusion, with the know-how and facilities of the catalyst producer FRAUENTAL KERAMIK, Austria. These honey combs were tested with a separate micro reactor, which was in use at the above mentioned company.

XPS data from literature show, that the Co content at the surface strongly depends on calcination temperature /19-21/. Therefore we varied additionally the calcination temperature of $LaCoO_3$ between 620 and 1150°C. Some calcined products were treated with water, because this significantly enhanced the catalytic activity. For comparison we included a commercial support coated with Pd (supplied by Kanzler Verfahrenstechnik, Austria) into our investigations.

RESULTS

Catalytic Properties

In the following figures all conversion/temperature curves refer to the gas inlet temperature, because the heat evolution during oxidation and thereby caused temperature distribution makes the kinetics a dynamical one. So self heating, formally acting as an autocatalytic reaction was the reason why we usually did not analyze the kinetics. But from several measurements approaching equilibrium temperatures, achieved with a smaller amount of catalyst and CO (reduced self-heating), we can roughly state, that up to a high degree the conversion curves correspond to an Arrhenius' law of activation, excluding a transport limitation in the gas phase up to about 300°C. It is remarkable that activation energies of such a variety of materials like $LaCoO_3$, $LaNiO_3$, Co_3O_4, prepared at different calcination temperatures are almost equal and amount to 0,6±10%eV (fig. 1).
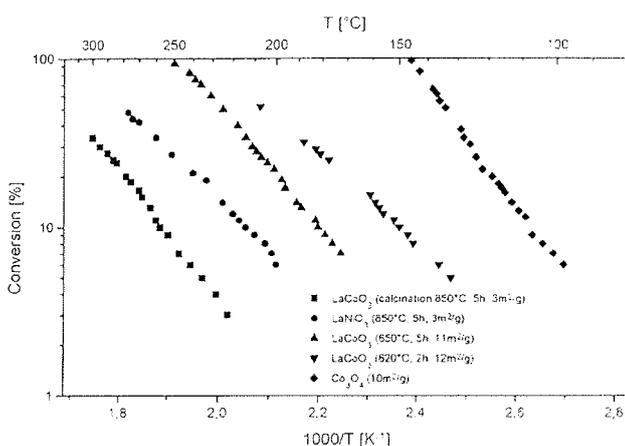

Fig. 1: Arrhenius' evaluation of conversion curves.

As can be noticed from fig. 2, one of the most CO active substances except Pd covered supports is Co_3O_4. CO/CO_2 conversion starts below 100°C and reaches values of 100% at about 140°C, whereas $LaCoO_3$ needs at least 50° higher inlet temperature. The conversion curves of the Ni and Al substituted $LaCoO_3$ materials display one common feature: the higher the Co content in the bulk and hence at the surface, the more active is the material. Because of the much higher Co content, Co_3O_4 fits well into this simple model.

A similar conclusion can be drawn from the conversion behavior of the honey combs and the reground honey combs, showing no essential difference. Such honey

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combs work like a mixture of powders. Furthermore, it does not matter, whether the ions substituted for Co in $LaCoO_3$ are active 3d-ions (Ni^{3+}) or not (Al^{3+}). But at this stage we cannot decide, which kind of Co ions with respect to valence and spin state at the surface is responsible for the catalytic oxidation. The support TiO_2/WO_3, which is the commercial basis for ceramic catalysts for NOx-reduction, is inactive for CO-oxidation and the activity depends only on the amount of $LaCoO_3$.
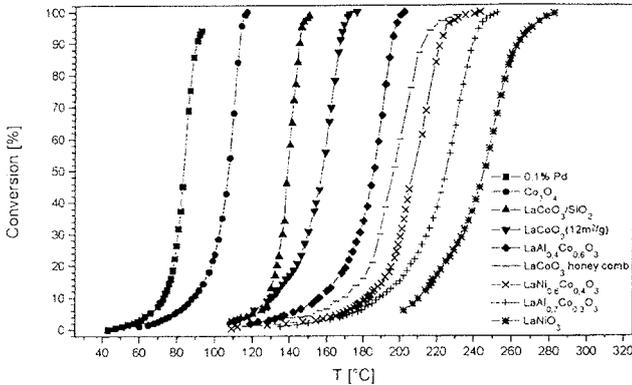
Fig. 2: Conversion curves of various materials (reactor filling 5 g).

Two preparation phenomena, which lead to a veritable increase of the catalytical activity are documented in figs. 3a and 3b. The first one concerns the calcination temperature and the second one the treatment of already calcined products with water. Calcination at lower temperatures leads to higher, surface-normalized reaction rates and treatment with water shifts the conversion curve to lower temperatures.

By normalization with respect to surface area for the conversion curves in fig.3a an activity ratio of 17:7:4 is found. X-ray analysis of these materials proved perovskite type structure and no additional impurity phases were found. For materials calcined at lower temperatures we assume, that these are more active because of unoxidized Co^{2+} species. On the other hand, the treatment with water (fig.3b) might have cleaning or dissolution effects, or the Co^{3+} ions are reduced to more active Co^{2+} ions approaching the case of Co_3O_4.
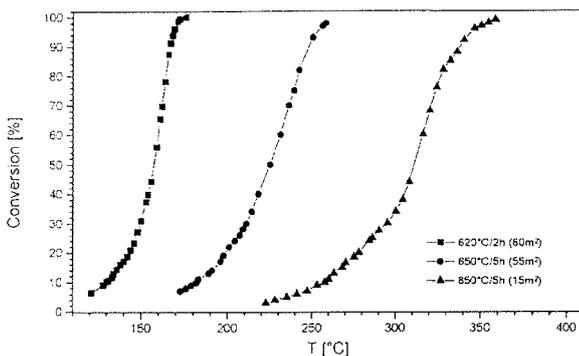
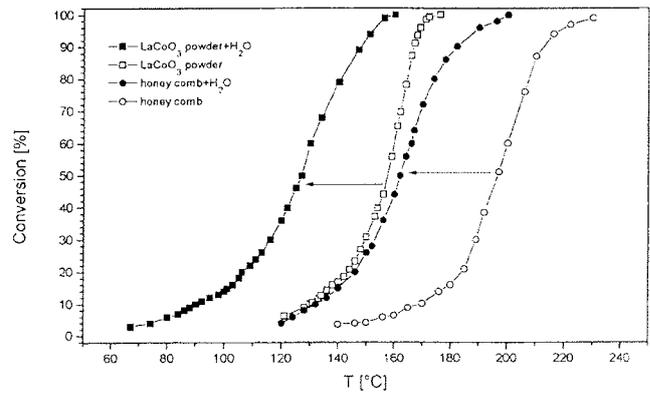Fig. 3a: Conversion curves of 5g $LaCoO_3$ calcined at different temperatures.

Fig. 3b: Shift of conversion curves by water treatment.

Some additional experiments were carried out with Sr^{2+}- and Ti^{4+}-substituted materials (fig. 4). Both the Sr^{2+} substitution of La^{3+} ions and the Ti^{4+} substitution of Co^{3+} ions shift the conversion to lower temperatures.

Here and in all other cases of Co and Ni containing catalysts the influence of SO_2 is extremely negative: The CO oxidation is completely stopped within a few minutes, indicating a lethal chemical adsorption of SO_2 or SO_3. As shown by $La_{0,8}Sr_{0,2}CoO_3$ in fig. 4 a certain but not total recovery is only achievable by heating up to temperatures above 600°C. Pd coated supports do not show this behavior and oxidize SO_2 into SO_3 in parallel to CO, even in a 2% O_2 containing gas.
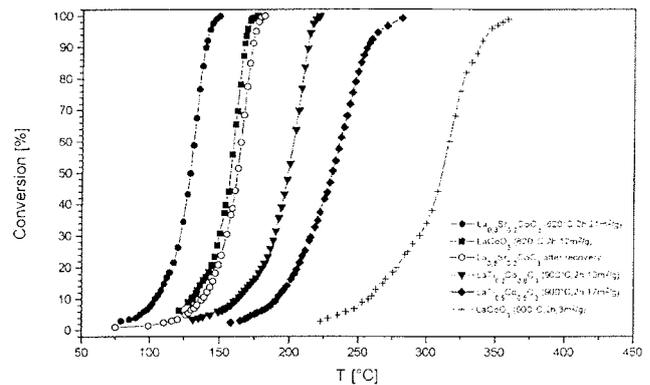
Fig. 4: Conversion influenced by substitution and SO_2 poisoning.

Electrical Properties

Referring to room temperature, the bulk conductivity of sintered pellets of the materials under investigation range from metallic (e.g. $LaNiO_3$) to semiconducting (e.g. $LaCoO_3$, $ZnNiMnO_4$) and low conducting materials (heavily Al and Ti doped $LaCoO_3$) (fig. 5).

In the catalytically interesting temperature range of 100 to 400°C, $LaCoO_3$ behaves semiconducting with an activation energy of about 0,55eV /22-24/. Above 400°C the behavior changes to a metallic type. Doping with Ti decreases the conductivity and increases the activation

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energy to about 0,6-0,7eV /25-28/. Co_3O_4 also behaves semiconducting, but with an activation energy changing from low to high temperatures (0,3-0,7eV) /29, 30/. On the other hand, in a wide range $LaNiO_3$ is a Pauli type metallic conductor /31, 32/.
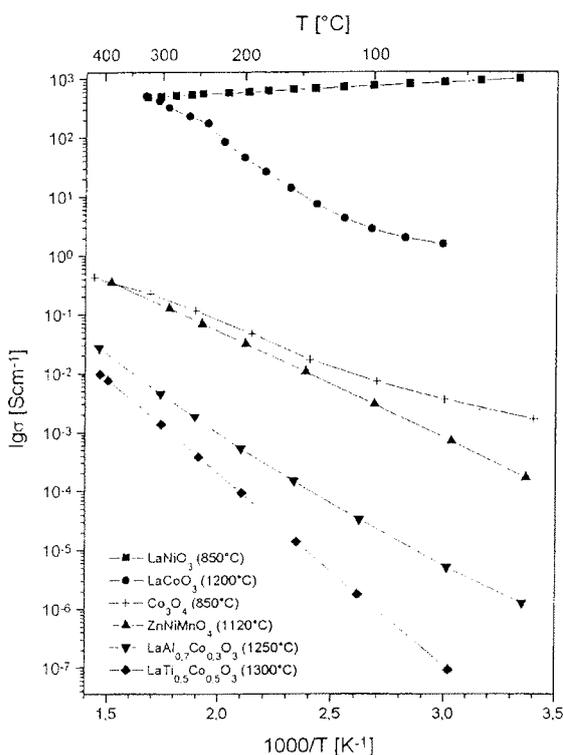
T [°C]

Fig. 5: *Conductivity data of some active materials.*

Most of the sintered Co and Ni containing materials conduct via activated hopping of electronic charges, i.e. small polarons. So one is tempted to assume, that the Arrhenius´ like conversion curves (fig. 1), which are proportional to the temperature dependence of the oxidation rate, are kinetically determined by the balance of hopping charges. Activation energies for hopping conduction and conversion rates are of the same order of magnitude (0,6 eV).

However, a simple inspection of the conductivity and activity data of $LaNiO_3$ reveals, that there is no direct correlation between electrical bulk and catalytical surface properties. This is also supported by the results obtained with Sr- and Ti-substituted $LaCoO_3$. As Sr-substitution increases the electronic conductivity and Ti-substitution decreases it, the enhanced catalytic activity in both cases shows that electronic conductivity does not have any influence on the conversion rate. So one is led to state, that bulk and surface regions are not coupled. If there is still an Arrhenius´ like temperature dependence, it must either be caused by a quite different activated step or by a charge transfer between Co^{2+} and Co^{3+} ions (Ni^{2+} and Ni^{3+} ions respectively) because of a restructured $LaCoO_3$ surface. In other words, we conclude, that in all cases the catalytic activity depends on a properly mixed valence state at the surface, as it is given in the case of the spinel Co_3O_4.

Magnetic Properties

Co_3O_4 is a mixed-valence compound with normal spinel structure. Co^{2+} ions are located at tetrahedrally and Co^{3+} ions at octahedrally oxygen coordinated lattice positions /33, 34/. It was first shown by Cossee /35/, that the observed magnetic susceptibility is consistent with a material, where Co^{2+} ions are high-spin (total spin S=3/2) with a spin-only moment of μ_{SO}=3.87μ_B (equ.1) and Co^{3+} ions are low-spin (S=0) because of the strong octahedral crystal field.

$$\mu_{SO} = \sqrt{4S(S+1)} \cdot \mu_B = 3{,}87\mu_B \qquad (1)$$

μ_{SO}:   spin-only moment
μ_B: Bohr magneton

The temperature dependence of the susceptibility (fig. 6) shows Curie-Weiss behavior (equ. 2). The evaluation including a diamagnetic correction with Pascal constants /36/ leads to an effective moment of μ_{eff}=4,57μ_B (equ. 3). The deviation from the spin-only value 3,87 can be attributed satisfactorily to spin-orbit coupling /35/.

$$\chi = \frac{C}{T - \Theta} \qquad (2)$$

χ: Susceptibility
Θ: Weiss-Temperature (-109K)
C: Curie Constant (2,607 cm^3Kmol^{-1})

$$\mu_{eff} = \sqrt{8C} \cdot \mu_B = 4{,}57\mu_B \qquad (3)$$

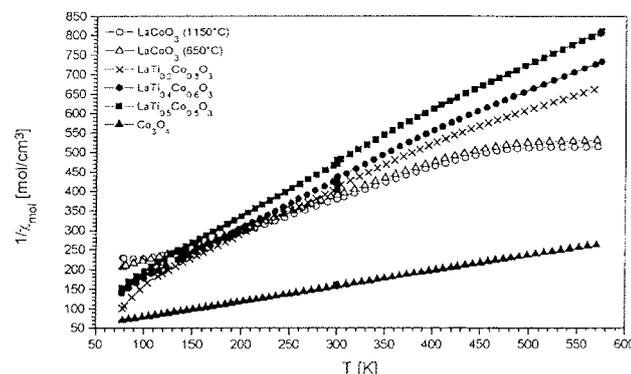μ_{eff} effective moment

Fig. 6: *Inverse molar susceptibilities.*

The low-temperature susceptibility (fig. 7 curve a) goes through a maximum at about 40 K (Neel-temperature), which is consistent with an antiferromagnetic ordering of Co^{2+} spins /34/. A Co_3O_4 sample exposed to 0,1% SO_2 under conversion conditions (45 min, 310°C) has the same Neel-temperature, but shows an increase of the magnetic susceptibility towards lower temperatures (fig. 7 curve b). The absence of a field dependence excludes the presence of ferromagnetic impurities in the exposed sample. The additional component is paramagnetic and most probably surface $CoSO_4$. The

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relative amount of $CoSO_4$ in the sample can be roughly estimated to about 0,2%, when the observed Curie constant of the paramagnetic component is compared with the one of $CoSO_4$.
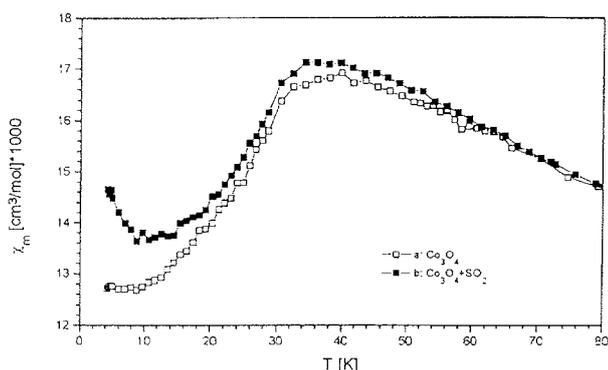

Fig.7: Low-temperature molar susceptibility of Co_3O_4 (a) and Co_3O_4 exposed to SO_2 (b)

On the other hand, Co^{3+} ions in $LaCoO_3$ occupy octahedral positions and their spin state changes in a wide temperature range /8, 9, 37/. The magnetic properties are governed by a subtle balance between the crystal field strength and the intra-atomic exchange energy, so that small temperature changes may cause conversion from low-spin to high-spin state and vice versa. The $1/\chi$ values of $LaCoO_3$ samples calcined at different temperatures are almost identical in the temperature range 150 to 600 K (fig 6). Above 400 K the inverse susceptibility reaches a temperature independent plateau, indicating a metal like phase /9, 38/. From 150 to 400 K the Curie-Weiss law applies, below 100 K severe discrepancies of the differently calcined materials occur. Samples calcined at temperatures above 900°C show a minimum in the $1/\chi$ curve, while those calcined below 900°C do not show a minimum. The $1/\chi$ curve decreases rapidly towards lower temperatures and a notable field dependence is observed indicating an additional ferromagnetic phase /9, 38, 39/.

The presence of this ferromagnetism, which dominates the low-temperature susceptibility excludes a direct observation of the paramagnetic surface $CoSO_4$ species in SO_2 exposed $LaCoO_3$ samples. Curie Constants, C, Weiss temperatures, Θ and effective moments, μ_{eff}, of a Curie-Weiss analysis with diamagnetic correction are given in table 1.

According to a recent reinvestigation of $LaCoO_3$ /9/ the following conclusions can be drawn. The calculated effective moment for a 1:1 mixture of low- and high-spin Co^{3+} ions is 3,46 μ_B, however, smaller values are found experimentally. The reason for this difference could either be due to the presence of less than 50% high-spin Co^{3+} ($\mu_{SO}=4,9$ μ_B) or to a partial replacement of the high-spin species by Co^{2+} ($\mu_{SO}=3,87$ μ_B) or to both at the same time. The fact that the samples calcined at lower temperatures give the smaller effective moments is consistent with a larger amount of surface Co^{2+}, which also explains the observed field dependence.

Table 1: Curie-Weiss analysis

Sample	C [cm³Kmol⁻¹]	Θ [K]	μ_{eff} [μ_B]
$LaCoO_3$ (1150°C/5h)	1,234	-158	3,14
$LaCoO_3$ (1050°C/5h)	1,240	-160	3,15
$LaCoO_3$ (950°C/5h)	1,229	-158	3,14
$LaCoO_3$ (850°C/5h)	1,211	-155	3,11
$LaCoO_3$ (750°C/5h)	1,204	-153	3,10
$LaCoO_3$ (650°C/5h)	1,194	-155	3,09
$LaTi_{0,2}Co_{0,8}O_3$ (900°C/2h)	0,888	-54	2,67
$LaTi_{0,4}Co_{0,6}O_3$ (900°C/2h)	0,837	-52	2,59
$LaTi_{0,5}Co_{0,5}O_3$ (900°C/2h)	0,762	-51	2,47
Co_3O_4	2,607	-109	4,57

For the catalytic activity of $LaCoO_3$ materials the existence of Co^{2+} at the surface is obviously of great importance. When the materials are calcined at lower temperatures a larger amount of unoxidized Co^{2+} species is retained causing higher activity (see fig. 3a). At the same time, treating the materials with water causes reduction of Co^{3+} to Co^{2+} thus, again enhancing the catalytic activity (see fig. 3b).

In the attempt to create Co^{2+} ions in $LaCoO_3$ we substituted Ti^{4+} for Co^{3+} ions. The inverse susceptibilities of three samples $LaTi_xCo_{1-x}O_3$ (x = 0,2, 0,4, 0,5) are also shown in fig. 6. Ti^{4+} is diamagnetic, hence a reduction of the susceptibility with increasing substitution is expected and is observed (table 1). The $1/\chi$ behavior is consistent with a metallic $LaCoO_3$ phase coexisting with paramagnetic Co^{2+} ions. The effective moment can be estimated according to

$$\mu_{eff} = \sqrt{x \cdot \mu_{SO}^2\left(Co^{2+}\right) + (1-2x) \cdot \mu_{eff}^2(LaCoO_3)} \cdot \mu_B$$

(4)

Insertion of 3,87 for Co^{2+} and 3,10 for $LaCoO_3$ leads to the values 2,95 for x = 0,2, 2,81 for x = 0,4 and 2,73 for x = 0,5. From chemical analysis we know, that the com-

Table 2: Chemical analysis of Co oxidation state in $LaTi_{1-x}Co_xO_3$ materials

Perovskite	Average Co oxidation state			BET surface of calcined materials [m²/g]
	nominal	observed		
		calcined 900°C	sintered 1250°C	
$LaCoO_3$ (620°C/2h)	3	2,86		12
$LaCoO_3$ (900°C/2h)	3	2,93		3
$LaTi_{0,2}Co_{0,8}O_3$	2,75	2,7	2,65	10
$LaTi_{0,4}Co_{0,6}O_3$	2,57	2,43	2,36	11
$LaTi_{0,6}Co_{0,4}O_3$	2,33	2,58	2,22	13
$LaTi_{0,8}Co_{0,2}O_3$	2	2,62	2,06	17

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position given by x is not really achieved by a heat treatment at 900°C (table 2). So we understand why the applied estimation gives too high moments, but the trend is well reproduced. The strong increase and the field dependence of χ below 100 K again indicate the presence of Co^{2+} at the surface.

DISCUSSION

Although XPS spectra show a Co deficit, when calcination is carried out at low temperatures, XPS cannot differentiate between Co^{2+} and Co^{3+} ions. So one needs additional arguments for the decision, which of the Co ions or possibly both together create catalytical activity at the surface. Because of the stoichiometry and spinel type structure of Co_3O_4 both ions are present to a high extent in the bulk and at the surface, whereas in $LaCoO_3$ only Co^{3+} ions exist in the bulk. In a well crystallized perovskite lattice Co^{2+}/Co^{4+} ion pairs can be created by temperature dependent disproportion of Co^{3+}, but to a much smaller amount.

Under the real conditions of preparation some unreacted Co^{2+} portions may remain, for example, when nitrates decompose, but do not react completely. Another possibility is given by a reducing treatment with aqueous solutions or by decomposition at too high temperatures leaving an oxygen deficiency. It was recently proved experimentally, that Co^{2+} ions are responsible for catalytical activity in Co_3O_4, which was prepared with different Co^{2+} content /40/. As the spinel is the much better CO catalyst than the perovskite, we suppose that both ions need to be present for a fast reaction, operating via charge transfer after a first O_2 adsorption step.

The implementation of Co^{2+} ions in $LaCoO_3$ by substitution of Ti^{4+} ions at the calcination-temperature 900°C enhances both the Co^{2+} content and the activity (table 2 and fig. 6). Thus we believe, that in all $LaCoO_3$ materials there is always a kind of mixed-valence surface phase present. The lower the calcination temperature the more mixed-valence states are formed. Moreover, the range of activation energy for electronic hopping process (0,4-0,7eV) fits well to the activation energy of the catalytical reaction (0,5-0,7eV).

CONCLUSIONS

From the experimental results of this work the following conclusions can be drawn. For any Co and Ni containing spinel or perovskite type material to be a good CO burning catalyst, it must contain mixed valences of 3d-ions at the surface, to facilitate a fast charge transfer when O_2/CO adsorption takes place.

It can be stated, that the catalytic activity is mainly influenced by the ratio of Co^{3+} and Co^{2+} at the surface of the material. A surface treatment of $LaCoO_3$ can be done by a partial reduction of already calcined products with aqueous solutions or calcination at low enough temperatures to get also large surface area. The limiting case of any improvement would be similar to the Co_3O_4 surface itself.

Although the activation energy of the CO oxidation corresponds to the activation energy of hopping

charges in the bulk, no direct correlation with the DC bulk conductivity is observed. On the other hand, the magnetic susceptibility of native $LaCoO_3$ powders, calcined at low temperatures, indicate directly the presence of high-spin Co^{2+} (mixed valence states).

As anticipated before, SO_2 is a very strong inhibitor and blocks the exceptionally fast CO reaction instantly. Most probably it is chemisorbed at oxygen covered Co^{2+} sites and leads finally to sulfate formation. Decomposition of pure $NiSO_4$ and $CoSO_4$ takes place around 800°C, so that the problem of recovery at lower temperatures is evident and all catalysts of this type fail in low temperature applications of SO_2 containing waste gases. Quite the same SO_2 problem appears with honey combs and impregnated supports, otherwise being as fast as Pd coated supports. The Pd catalyst withstands SO_2, but during CO/CO_2 reaction it is oxidized to SO_3.

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ACKNOWLEDGEMENT