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Relation Between the Physicochemical, Electronic and Catalytic Properties of Nickel Oxide Doped with Chromium

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Catalytic activity of CO to CO_2 oxidation for polycrystalline nickel oxide doped with chromium has been investigated. Both electronic and thermodynamic factors of the $NiO–Cr_2O_3$ catalysts has been studied using thermoelectric power, electromotive force (emf) of the solid galvanic cell and contact potential difference (cpd). The difference between surface and bulk properties of $NiO–Cr_2O_3$ solid solution has been stated. The catalytic activity was found to be correlated with the surface electronic properties of the system under investigation.

1. INTRODUCTION

One of the methods widely applied for changing the electronic state of semiconducting catalysts consists of the introduction into their parent lattice of altervalent ions. Such doping must yield homogeneous solid solutions if one is to compare experimental results with theoretical predictions.

In preceding studies on physicochemical and catalytic properties of nickel oxide doped with lithium (i.e., on solid solutions $NiO–Li_2O$) it has been shown that the lithium addition affects the bulk and surface properties of polycrystalline (*1*) and monocrystalline (*2*, *3*) samples of NiO in different ways. In all cases, however, parallel changes of the Fermi level position at the surface and catalytic activity in the model reaction of oxidation of CO to CO_2 were observed for the samples of different concentrations of the additive introduced.

In the case of a trivalent additive introduced into the NiO lattice the results obtained in different laboratories differ considerably (*4–10*). In our opinion this is due among other factors to the fact that the preparation of homogeneous solid solutions of trivalent metal oxides such as Fe_2O_3, Ga_2O_3, or Cr_2O_3 in NiO is difficult. Moreover, in the $NiO–M_2O_3$ (M = metal) systems composite oxides may be formed. As shown previously, introduction of gallium leads to the formation of a heterophase mixture in which gallium is incorporated into NiO lattice only to a very small extent (*5*, *11*). A similar situation occurs also in the case of nickel oxide doped with iron (*10*). It seemed of interest, therefore, to prepare homogeneous solid solutions in the $NiO–Cr_2O_3$ system and to investigate the effect of chromium addition on physicochemical and surface properties of such preparations. In order to compare the changes in the properties which occur in this case with those occurring when $NiCr_2O_4$ spinel is formed, the chromium-rich preparations which are a heterophase mixture have been also investigated. According to Hauffe (*12*) the formation of the solid solutions of Cr_2O_3 is accompanied by the formation of donors in the NiO lattice. This process may be written as follows:

$$Cr_2O_3 + 3Ni^{*}_{Ni} \rightarrow 2Cr^{\cdot}_{Ni} + V''_{Ni} + 3NiO. \quad (1)$$

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Meier and Rapp (*13*) assume that the first stage of the reaction consists of the formation on the surface of NiO grains of $NiCr_2O_4$ spinel. The spinel is then dissolved in the NiO lattice according to the equation:

$$NiCr_2O_4 \rightarrow Ni^{*}{}_{Ni} + 2Cr^{\cdot}{}_{Ni} + 4O^{*}{}_{O} + V''{}_{Ni}. \quad (2)$$

In both of the above cases introduction of chromium leads to the formation of donor centers, i.e., to the rise of the Fermi level. The following experimental methods have been applied in the present studies:

a. Electromotive force (emf);
b. Thermoelectric power (α);
c. Work function (cpd);
d. Catalytic activity in the CO oxidation reaction.

2. Experimental

A. *Materials*

A detailed description of the preparation method was given earlier (*14*). The synthesis consisted of coprecipitating nickel and chromium hydroxides with $2\,M$ ammonia from $1\,M$ solutions of $Ni(NO_3)_2$ and $Cr(NO_3)_3$ in appropriate proportions. After a preliminary drying at 120°C the precipitates of the hydroxides were decomposed in a stream of oxygen at 500°C and then calcined in Alundum crucibles at 1100°C for about 10 hr.

The preparations obtained were analyzed by zone dissolution of the samples and by determination of amount of chromium and nickel ions dissolved. $4\,N$ HCl was used as a solvent since it did not dissolve Cr_2O_3 and $NiCr_2O_4$. The samples containing up to 2.04 at.% Cr were completely soluble and fractional analysis confirmed their homogeneity. The samples of higher concentration of chromium did not dissolve completely: they were a heterophase mixture of NiO containing about 1 at.% of incorporated chromium, and of the spinel. This is shown in Fig. 1, taken from (*14*), in which the amount of chromium incorporated into the NiO lattice is plotted as a function of the amount of chromium introduced. As shown in this plot the maximum concentration of the solution in the preparation conditions adopted amounts to about 1 at.% Cr. The sample containing 2.04 at.% Cr is believed to be a supersaturated solution. The studies were performed on samples containing 0.02, 0.19, 0.55, 1.07, 2.04, 4.55 and 10 at.% Cr. The detailed X-ray studies and preparation of the specimens were described in the previous paper (*14*). The problem of the supersaturated solution of Cr_2O_3 in NiO is the subject of further investigations. The specific surface areas of the preparations are ~1.7 m^2/g irrespective of the concentration of the additive introduced. Spectral and photometric analysis showed the presence of Al and Cu not exceeding 0.001% and traces of Ti, Ca, Si, Mg. No alkali metals were found in the samples.

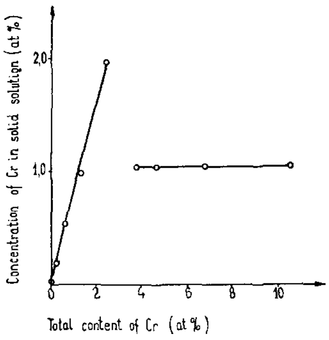

FIG. 1. Dependence of the amount of chromium incorporated into the NiO lattice on the amount introduced after (*14*).

$NiCr_2O_4$ spinel was also synthesized by heating the equimolar mixture of the oxides at 1100°C for 10 hr. The specific surface area of this preparation was 5.0 m^2/g.

B. *Methods*

a. *Measurement of Electromotive Force (emf) of Solid Galvanic Cells*

In order to determine enthalpy and entropy of formation of $NiO–Cr_2O_3$ solid solutions, the electromotive force of solid galvanic cells given by the scheme,

$$(+)\ Pt|Ni,NiO\left\|\begin{matrix}\text{solid}\\ \text{electrolyte}\end{matrix}\right\|Ni,(NiO + Cr_2O_3)|\ Pt\ (-), \quad (3)$$

was measured.

The left side half-cell consisted of a

tablet made of an equimolar mixture of spectrally pure nickel and polycrystalline nickel oxide. The right side half-cell was a tablet of an equimolar mixture of metallic nickel and the preparations of NiO containing Cr_2O_3 described above. The solid solution of CaO in ZrO_2 (molar ratio, 17:3) was used as solid electrolyte (*15*). The emf measurements were determined in the temperature range from 700 to 900°C in an atmosphere of argon. The detailed description of the apparatus and the experimental method are given elsewhere (*16*).

b. *Measurement of Thermoelectric Power*

In order to study the effect of the chromium addition on the position of the Fermi level in the bulk of the crystallites, measurements of the thermoelectric power (α) were made. These were carried out in air at 500°C, using pellets. The apparatus and the method of the measurements were described earlier (*17*).

c. *Measurement of Electron Work Function*

The measurements of the electron work function were aimed at the determination of the changes of the Fermi level position, E_F, at the surface as a function of the chromium additive concentration. The change of the negative values of the contact potential difference (cpd) in this case is a direct measure of the change of the Fermi level position at the surface. The cpd measurements were carried out in oxygen at a pressure of 10 mm Hg at 400°C with the dynamic capacitor method (*18*). Platinum was used as the reference electrode. With appropriate standardization of the reference electrode (*19*) its work function was practically independent of the oxygen pressure and was constant under the experimental conditions applied. Hence the measured changes of the cpd were equal to the changes of the work function of the oxide specimens. The measurement temperature was selected in such a way as to work in the range of reversible changes of the work function values in the oxygen adsorption–desorption cycles (*20*).

d. *Catalytic Properties*

Oxidation of carbon monoxide has been chosen as a catalytic test reaction. Catalytic measurements were carried out in the temperature range 200–400°C, using a circulation system. The system included a liquid air trap in which CO_2 was frozen out. The reaction was followed by registering the change of pressure. The initial pressure in the reactor was 30 Torr in all experiments. The reaction was carried out with the ratio $CO/O_2 = 1$, i.e., in an oxygen excess with respect to stoichiometry of the reaction. The excess of oxygen was used to prevent changes in composition of the near-to-surface layers during the catalytic reaction (*21*) (changes in coverage with chemisorbed oxygen). In all the experiments the same sequence of admitting the gases to the reaction chamber was maintained. After standardization of the catalysts in 15 Torr O_2 at 450°C oxygen was introduced first to the reactor and then the appropriate amount of CO was added. The details of the standardization method and the measurement procedure are given elsewhere (*22*).

Before the measurements the reaction order was determined. In all cases the reaction order with respect to oxygen was zero and the first order with respect to CO. The reaction rate could be therefore described by the following equation:

$$v = k_0 p_{O_2}{}^0 p_{CO}{}^1 = k_0 p_{CO}. \qquad (4)$$

3. Results of the Investigation

At any given temperature a constant value of emf was obtained after about 20 min. In the temperature range studied the galvanic cell was reversible: the same values of emf were obtained approaching the measurement temperature both from the high and low temperature sides. For illustration of the results obtained, Fig. 2a shows the dependence of the stationary values of emf on the concentration of Cr_2O_3 added for the temperature of 900°C. The values observed for heterophase mixtures are joined with broken lines (the same applies to Figs. 3–6 below). Analogous dependences were observed in the whole tem-

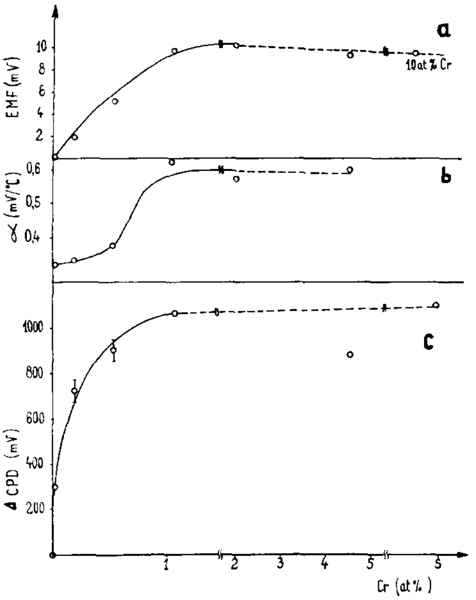

FIG. 2. Dependence of: (a) electromotive force of cells described by scheme (3), (b) thermoelectric power, and (c) contact potential difference changes (cpd) measured at 400°C and 10 mm Hg of oxygen vs concentration of chromium addition; *s* denotes the $NiCr_2O_4$ spinel. The values for heterophase mixtures are joined with broken lines.

perature range under study. With an increase in the additive concentration up to about 2 at.% Cr, the emf value increases and then remains constant.

The results of the thermoelectric power investigation are given in Fig. 2b. As for the emf measurements α increases initially (up to about 1 at.% Cr) and then at higher Cr contents it remains constant.

Figure 2c presents the results obtained in the work function measurements. The experimental point for the sample containing 2.04 at.% Cr_2O_3 (supersaturated solution) is omitted because the reproducibility of the results was considerably worse than that for the other samples. The work function value for this sample was much lower than that which could be expected from the illustrated course of Δcpd vs concentration of chromium (in Fig. 2c) and was equal to about 400 mV. The plot obtained is similar to those given in Fig. 2a and b. The cpd increases rapidly up to a chromium content of 1 at.% and reaches a constant value at higher concentrations of chromium. This constant work function value is close to that of the spinel $NiCr_2O_4$.

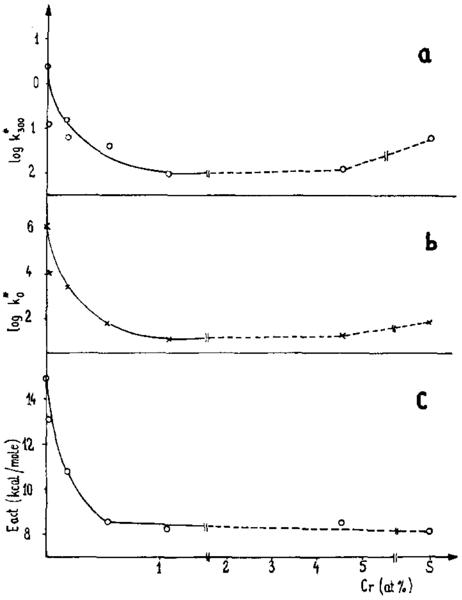

FIG. 3. Dependence of: (a) log k^*, (b) log k^*_0 (reaction temperature 300°C), and (c) activation energy of oxidation of CO on the concentration of the chromium addition.

The kinetics obey the Arrhenius equation:

$$k = k_0 \exp(-E_{act}/RT). \quad (5)$$

The values of the constants k and k_0 referred to unit surface (k^* and k^*_0) and the apparent activation energy E_{act} for different concentrations of Cr are illustrated in Fig. 3.

All the parameters given above first decrease with increasing Cr concentration and then reach constant values. Similar values are observed for the synthesized spinel. It is worth mentioning that the sample containing 2.04 at.% Cr, i.e., that which may be regarded as a supersaturated solid solution and for which the marked rise in the surface Fermi level position was observed, showed practically no activity in the oxidation. Owing to this fact the points corresponding to this sample are not given in Fig. 3.

Leaving aside the 2.04 at.% Cr sample, the Constable equation,

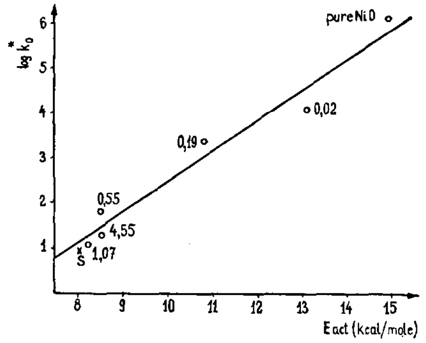

FIG. 4. Dependence of log k^*_0 on E_{act}. The numbers at the points denote the chromium content (at.%).

$$\log k^*_0 = \mathrm{A} + \mathrm{B}E_{act}, \qquad (6)$$

is obeyed to a good approximation (see Fig. 4), with A and B equal to 4.32 and 0.68, respectively.

4. Discussion

The partial molal enthalpy $\overline{\Delta H}$ and entropy $\overline{\Delta S}$ occurring during the incorporation of chromium into the parent lattice of NiO were calculated from the emf results. The calculation can only be performed realistically for the preparations containing solid solutions, i.e., the samples for which the chromium concentration did not exceed about 2 at.%, but to show the effect of the heterophase presence of $NiCr_2O_4$ the calculations were also done for higher concentrations of chromium. The results are illustrated in Fig. 5 and in Table 1.

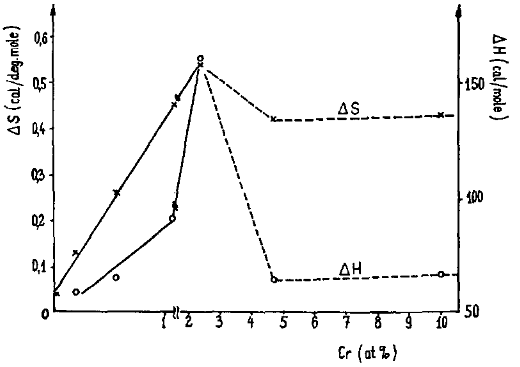

FIG. 5. Dependence of $\overline{\Delta S}$ and $\overline{\Delta H}$ of NiO in solid solution on the concentration of the incorporated chromium.

TABLE 1

THE VALUES OF TEMPERATURE COEFFICIENTS OF EMF OF THE CELL[a]

Chromium concn (at.%)	$b \times 10^3$ (mV/°C)	$b \times 10^3$ (mV/°C)
0.19	2.71	0.043
0.55	5.64	0.090
1.07	9.75	0.22
2.04	11.60	0.44
4.55	9.11	1.00
10.0	9.32	2.35

[a] + Pt|Ni,NiO||solid electrolyte||Ni,(NiO + Cr_2O_3)|Pt (−).

The emf of the cell given by scheme (3) is due to the following reaction,

$$\mathrm{NiO} \rightarrow (\mathrm{NiO})_{ss} \qquad (7)$$

where NiO, $(NiO)_{ss}$ denote, respectively, pure NiO and NiO in solid solution. The free energy change ΔG is equal to the partial molal free energy $\overline{\Delta G}$ of NiO in solid solution,

$$\Delta G = \Delta G_{ss} - \Delta G_{\mathrm{NiO}}{}^0 = \overline{\Delta G}, \qquad (8)$$

which is related to the emf E by

$$\overline{\Delta G} = -2\,FE. \qquad (9)$$

Since emf is a linear function of T for all the solid solutions investigated, we may write

$$E = a + bT, \qquad (10)$$

where a and b are constants.

It is possible to calculate the temperature coefficients b and to refer them to the partial molal entropy of NiO in the solid solutions. Making use of Eqs. (9) and (10) and the relation $(\partial\overline{\Delta G}/\partial T)_p = -\overline{\Delta S}$, we obtain:

$$b = \left(\frac{\partial E}{\partial T}\right)_p = -\frac{1}{2F}\left(\frac{\partial\overline{\Delta G}}{\partial T}\right)_p = \frac{\overline{\Delta S}}{2F}. \qquad (11)$$

On the other hand, the same coefficients may be calculated from the configurational entropy S_{conf} where

$$\begin{aligned} S_{\mathrm{conf}} &= x(\bar{S}_{\mathrm{conf}})_{\mathrm{NiO}} + (1-x)(\bar{S}_{\mathrm{conf}})_{Cr_2O_3} \\ &= -R[x\ln x + (1-x)\ln(1-x)] \qquad (12) \end{aligned}$$

From Eqs. (11) and (12) we obtain:

$$b_{\mathrm{calc}} = \frac{(\bar{S}_{\mathrm{conf}})_{\mathrm{NiO}}}{2F} = -\frac{R\ln x}{2F}, \qquad (13)$$

where x is the molar fraction of NiO in the solid solutions. Knowing the $\overline{\Delta G}$ and $\overline{\Delta S}$ data the partial molal enthalpy for NiO $\overline{\Delta H}$ can be calculated. The values of the temperature coefficients obtained experimentally and by calculation are given in columns 2 and 3 of Table 1. As shown in the Table, the experimental values of b differ by about one order of magnitude from those calculated. This indicates that the investigated solid solutions can be regarded as nonregular. Values of both $\overline{\Delta S}$ and $\overline{\Delta H}$ increase in the preparations containing up to about 2 at.% Cr, i.e., in the range of solid solution. In the region of the heterophase system they assume practically constant values close to that observed for the solid solution containing about 1 at.% of incorporated chromium. Such results suggest that the spinel formed in this range of Cr concentration does not affect the calculated values of $\overline{\Delta S}$ and $\overline{\Delta H}$.

On the basis of the thermoelectric power measurements (Fig. 2b) and bearing in mind the relation,

$$\alpha = \frac{\mu - E}{Te}, \qquad (14)$$

where α	thermoelectric power
μ	Fermi level position in the bulk
E	energy of the level at which the transport of current carriers takes place (it is assumed that conduction in NiO takes place in the $3d^8$ band)
T	temperature
e	elementary charge,

it may be concluded that in agreement with the current viewpoints the chromium incorporated into NiO induces the formation of donor centers, thereby raising the Fermi level with respect to its position in pure NiO.

The results of the thermoelectric power measurements obtained for preparations with higher contents of Cr seem to indicate that in this case also the spinel formed does not affect the value characteristic of the saturated solution of Cr_2O_3 in NiO. Another picture is obtained from the work function data. The increase of the work function denotes the decrease of the Fermi level. As shown in Fig. 2c, the surface Fermi level is rapidly lowered with increase in the concentration of Cr up to above 1 at.% Cr. For the sample containing 2.04 at.% of Cr_2O_3 and interpreted here as a supersaturated solution, the value of the Fermi level is higher than that of the saturated solution. However, this value is lower than that obtained for undoped NiO. At higher concentrations of chromium no marked changes of cpd (Fig. 2c) are observed, its value for the solid solution of the highest concentration being practically equal to the value obtained for the spinel.

The facts given above may be interpreted in the simplest way if we assume that despite the apparent homogeneity of the samples, chromium is incorporated in the near-to-surface layers forming a defect structure of spinel-like type. This would be supported by the mechanism proposed by Meier and Rapp (*13*) for the incorporation of chromium described by Eq. (2).

From the results of thermoelectric power and cpd measurements presented above, it follows, irrespective of the interpretation assumed, that the chromium addition produces the formation of donor centers in the bulk of NiO crystals and that an opposite effect is observed for the near-to-surface layers. The picture obtained is then analogous to that observed in the case of the Li_2O–NiO system (*1*); introduction of the chromium addition to NiO gives rise to opposite electronic effects in the bulk and in the near-to-surface layers of the crystals.

The lowering of the activation energy E_{act} with Cr concentration (Fig. 3) is in agreement with the results obtained by Parravano (*7*) and Roginski, Keier and Sazonova (*9*). The opposite effects were observed by Schlosser and Herzog (for NiO with Ga addition) (*4*), Komatsu and coworkers (for NiO with addition of indium) (*23*), Bielański, Dziembaj, and Słoczyński (for NiO with addition of Fe) (*24*) and Schwab and Block (for NiO with addition of chromium) (*8*). The reaction orders with respect to CO and O_2, on the other hand, agree with those of Schlosser and Herzog (*4*), Dry and Stone (*6*), Schwab and Block (*8*) and Komatsu *et al.* (*23*). Only Bielański, Dziembaj and Słoczyński (*24*) have observed zero order with respect to both oxygen and carbon monoxide.

The preparation method applied in the papers quoted above were different and it is difficult to compare the results obtained by different authors since no detailed characteristics of the preparations studied were given. The difference between the results given by different authors can be also due to the differences in the initial composition of the reaction mixture. It has been shown previously (*21*) that the mechanism of the reaction may change with a change in the composition of the reacting mixture. In the case of the mixtures containing even a small excess of CO a partial reduction of the surface may take place.

5. CONCLUSIONS

The results presented above allow the following conclusions to be formulated.

1. The synthesis of NiO samples with the addition of chromium indicates that homogeneous solid solutions may be obtained only at relatively low concentrations of chromium.

2. These solutions may be assigned thermodynamically as nonregular solutions.

3. Introduction of Cr causes a rise in the Fermi level position in the bulk of the crystallites; the opposite effect on the other hand is observed on the surface, namely a lowering with an increase in the Cr concentration.

4. Introduction of the chromium causes a decrease of the activation energy of oxidation of CO to CO_2. A similar decrease is observed also in the values of k and k_0.

5. In the studied temperature range the reaction is of zero order with respect to oxygen and of first order with respect to CO.

6. Comparison of the work function and emf values obtained for doped NiO with the values for the spinel suggest the formation of spinel-like structure in the close-to-surface layers of NiO crystallites.

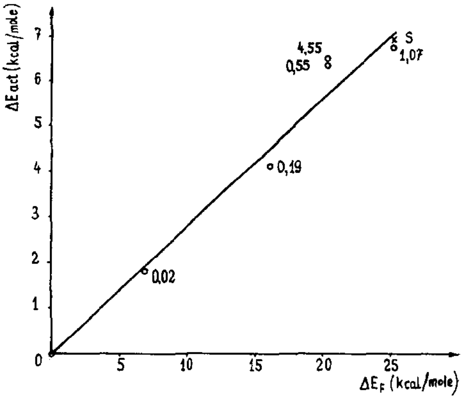

FIG. 6. Dependence of ΔE_{act} on ΔE_F.

7. It has been shown that the shape of the curve representing the dependence of E_{act} on chromium concentration is similar to the analogous dependence of the Fermi level position on the surface. This parallelism may be shown by plotting ΔE_{act} against ΔE_F (Fig. 6) where ΔE_{act} is the difference between the activation energy of a given Cr-doped sample and that of pure NiO, and $\Delta E_F (\Delta E_F = -\Delta\Phi)$ is the corresponding difference of the Fermi level values on the surface.[‡] The plotted straight line can be described by the equation,

$$\Delta E_{\text{act}} = 0.28 \Delta E_F. \tag{15}$$

Formally the reaction may be classified as a donor or *p*-type reaction (using the definition proposed by Volkenstein (*25*). This result is in agreement with those obtained by the other authors with the exception of Parravano (*7*) who considers oxidation of CO to CO_2 on NiO as an acceptor process. In our previous studies on catalytic properties of the NiO–Li_2O system the donor character of the reaction in question was also observed.

8. The results reported in the present work indicate clearly that even in the case of a simple reaction occurring on a simple catalyst, a detailed knowledge of many parameters characterizing the whole system is required before the correlation between the physicochemical and catalytic properties can be formulated.

[‡] $\Delta\Phi$ is the difference between the values of the work function for pure and Cr-doped samples.

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