Determination of non-stoichiometric oxygen in NiO by temperature-programmed reduction

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Nickel oxide samples, calcined at various temperatures, have been studied by temperature-programmed reduction to determine quantitatively the amount of non-stoichiometric oxygen both in the surface and in the bulk.

Keywords: Temperature-programmed reduction (TPR); non-stoichiometric oxygen; nickel oxide

1. Introduction

Depending on the mode of preparation, the calcination temperature in particular, NiO samples of various surface area, colour, and degree of non-stoichiometric oxygen and Ni^{3+} ions, can be formed. Upon temperature-programmed reduction (TPR) such samples yield a main peak at about 673 K, ascribed to the $Ni^{2+} \rightarrow Ni^0$ reduction. There is another less-intense peak at about 473 K which has been attributed [1,2] to a phase transfer from rhombohedral to cubic structure of the NaCl type. Other authors have assigned this peak to the reduction of traces of Ni^{3+} (Ni_2O_3) [3,4].

The present work aims to show how the TPR method can be used for evaluation of the non-stoichiometric oxygen in nickel oxide samples prepared under various conditions.

2. Experimental

Nickel oxide samples were prepared by precipitation of $Ni(NO_3)_2$ and ammonia. After washing, the precipitate was calcined for 4 h at 1073, 873 and 673 K (denoted as Ni(1073), Ni(873) and Ni(673), respectively). The differential thermal

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analysis (DTA) of the Ni(673) sample up to 673 K indicated no traces of undecomposed nitrates after calcination, which means that the TPR peaks were due exclusively to hydrogen consumption. All the measurements were carried out by means of an apparatus described elsewhere [5]. A cool trap, 233 K, for removing water during reduction was mounted in the gas line ahead of the thermal conductivity detector. A hydrogen–argon mixture (13% H_2), passed over a molecular sieve at 233 K, was used to reduce the samples at the flow rate of 24 ml min^{-1}. The temperature was linearly raised at the rate of 15 K min^{-1}. A quartz reactor was applied which was loaded with 0.02 g of material. All the experimental conditions mentioned above conformed with the equation of Monti and Baiker [6],

$$K = S_0 / V^* c_0 ,$$

where K is the characteristic number (s), S_0 is the initial amount of reducible species (μmol), V^* is the total flow rate of the reducing gas ($\text{cm}^3\ \text{s}^{-1}$), and c_0 is the initial hydrogen concentration (μmol cm^{-1}). For reasonable TPR data $55 < K < 140$ is required.

To determine the non-stoichiometric oxygen, the Ni^{3+} ions were reduced to Ni^{2+} by concentrated hydrochloric acid, the released chlorine being determined iodometrically. Hereafter, this method is referred to as the titrimetric one.

3. Results and discussion

Fig. 1 shows TPR spectra of the investigated samples. The low-temperature peak (fig. 1, curve A) was not observed with sample NiO(1073) which means that this sample did not contain non-stoichiometric oxygen, Ni^{3+} ions respectively. TPR spectra of the NiO(873) and NiO(673) samples exhibited peaks with maxima at 411 and 437 K, respectively, which are due to non-stoichiometric oxygen from the surface layer. Furthermore, we assign the peaks at $T_{\text{max}} = 506$ K and $T_{\text{max}} = 498$ K (curves B and C, respectively) to non-stoichiometric oxygen in the bulk. Preliminary treatment of a NiO(673) sample by temperature-programmed desorption (TPD) to 573 K in a flow of moisture-free and oxygen-free helium gave rise to a weak peak with T_{max} at 393 K (curve D). We attribute this peak to non-stoichiometric oxygen that has diffused from the bulk to the surface.

The following experiment was also performed with the NiO(673) sample. This sample was subjected to temperature-programmed oxidation (TPO) to 573 K and kept for 30 min at the same temperature. The oxidation mixture contained 10% oxygen in helium whereas the heating rate was 15 K min^{-1}. After cooling, a TPR measurement was conducted with the same sample (curve E). The peak with $T_{\text{max}} = 433$ K, which we assign to surface non-stoichiometric oxygen, strongly increased in intensity. The peak with T_{max} at 508 K, due to bulk non-stoichiometric oxygen, did not undergo changes while the peak with $T_{\text{max}} = 633$ K, ascribed to stoichiometric oxygen (Ni^{2+} ions), strongly decreased at the expense of the peak

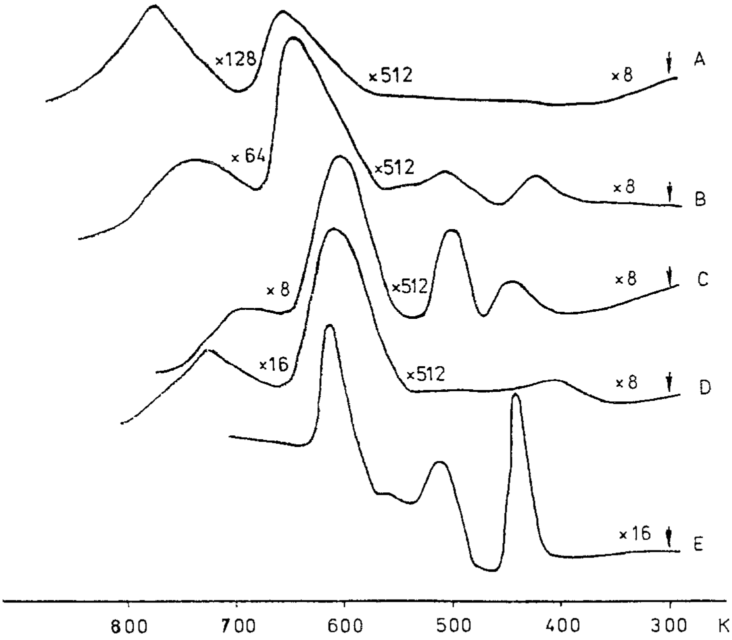

Fig. 1. TPR spectra of nickel samples: (A) NiO(1073) sample; (B) NiO(873) sample; (C) NiO(673) sample; (D) NiO(673) sample preliminary subjected to TPD to 573 K; (E) NiO(673) sample preliminary subjected to TPO to 573 K and kept for 30 min at the same temperature.

with $T_{max} = 433$ K. Thus, we attribute the former low-temperature peak ($T_{max} = 433$ K) to non-stoichiometric oxygen in the surface and the latter low-temperature peak ($T_{max} = 508$ K) to non-stoichiometric oxygen in the bulk of the oxide.

Finally we compared the quantitative TPR data with the amounts of non-stoichiometric oxygen determined by the chemical titrimetric method (table 1).

There is a satisfactory coincidence between the data derived from the two methods, but the TPR technique is easier and faster to distinguish quantitatively between surface and bulk non-stoichiometric oxygen.

All the TPR spectra exhibit a main peak in the 613–633 K range which is due to the $Ni^{2+} \rightarrow Ni^0$ transition. However, one more high-temperature peak with T_{max} in the 673–753 K range also appeared in some of the experimental runs. Its area was enlarged with the samples calcined at a higher temperature. The origin of the latter

Table 1
Non-stoichiometric oxygen determined by TPR and titrimetrically

Sample	Non-stoichiometric oxygen (at%)			
	TPR			Bunsen–Rupp total
	surface	bulk	total	
Ni(1073)	0.00	0.00	0.00	0.00
Ni(873)	0.07	0.05	0.12	0.11
Ni(673)	0.11	0.21	0.32	0.25

peak can be explained in the following way. During the reduction process the "nucleation" mechanism changes to the "contracting sphere" mechanism. According to this the diffusion of hydrogen into the interior of the grain as well as the diffusion of oxygen from the bulk to the surface is impeded because of the metal cover formed. In addition, we found that the latter peak grew in intensity with the rise of the calcination temperature. It is reasonable to suggest that the higher the temperature of formation of the oxide, the much closer to the stoichiometry its composition is. Therefore, there should be less defects and the crystal lattice should be more stable.

By using the proposed method, one can readily measure the non-stoichiometric oxygen in nickel oxide samples and correctly distinguish between bulk and surface non-stoichiometric oxygen.

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