Journal of Thermal Analysis and Calorimetry, Vol. 62 (2000) 345–348

NEW PROSPECTIVE Ni-CATALYTIC MATERIALS

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Abstract

IR spectroscopy was applied to investigate the non-isothermal redox processes in Ni/NiO–gas phase system involving the elimination of CO_2. At the Curie temperature (T_c=633 K for Ni), a change in the mechanism of CO catalytic oxidation on NiO was observed. It was established by means of temperature-programmed desorption with mass-spectroscopic registration that fluctuations in the oxygen density on the NiO surface are generated at this temperature. Under the given chemical reaction conditions, these fluctuations bring about the formation of Ni microheterogeneity on the NiO surface. X-ray diffraction, electronic and magnetometric measurements were employed to determine the dimensions of the Ni particles. It was shown that an increase in the Ni dispersity in Ni/NiO may be responsible for an increased number of active surface sites. This was verified for the NiO/thermo-exfoliated graphite system.

Keywords: catalysis, Curie temperature, nickel, temperature-programmed desorption, thermo-exfoliated graphite

Introduction

The structure of the active sites present in heterogeneous catalysts is of importance in catalysis. A change in the active site structure brings about change in the reaction mechanism. Ni and Ni compounds supported on carriers are used both for technology and for theoretical research. In the theory of catalysis, study of the influence of the carrier on the disperse and surface energy of a supported catalyst, and thereby on the active site structure and catalytic activity, is important [1, 2].

It is well known that two mechanisms of CO catalytic oxidation on NiO exist. These mechanisms are manifested at different temperatures and have substantially different activation energies. At high temperature, the mechanism of oxidation-reduction of the catalyst surface is realized; at low temperature, the associative mechanism is observed. The nature of this mechanism change has not yet been clarified. The change in mechanism occurs at 623–673 K. For the solution of this problem, it is necessary to use temperature-programmed desorption (TPD) with mass-spectroscopic registration, ESCA, X-ray diffraction, electronic and magnetometric methods.

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1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Two kinds of systems containing nanoscale Ni particles were prepared and studied: Ni particles grown on NiO surfaces by the reduction of NiO with CO at 623–703 K, and Ni particles chemically deposited on the surface of thermo-exfoliated graphite (TEG).

The reaction of catalytic CO oxidation on NiO and the reaction of NiO reduction with CO were studied in the closed set-up with a circulating argon flow. Pulse injection of the reactants was performed. The product concentration (CO_2) in the IR cell (cell length 10 cm) was determined with an IR spectrometer (Specord 71). A sensitivity in excess of 10^{-7} mol l^{-1} was obtained. TPD with mass-spectroscopic (MI-1201) registration was used to study the removal of O and O_2 from NiO. The surfaces of NiO and NiO/TEG catalysts were analyzed by ESCA (Kratos 800XPS). By means of X-ray diffraction, electronic and magnetometric measurements, the average size of the Ni particles in both systems was determined.

Results and discussion

A change in the mechanism of catalytic CO oxidation on NiO was found to occur at 633 K (Fig. 1, curve 2). At high temperature, the mechanism involves the alternate oxidation–reduction of the catalyst surface; at low temperature, the associative mechanism is observed. The associative mechanism includes the adsorption of components on the catalyst surface, the following reaction and product desorption.

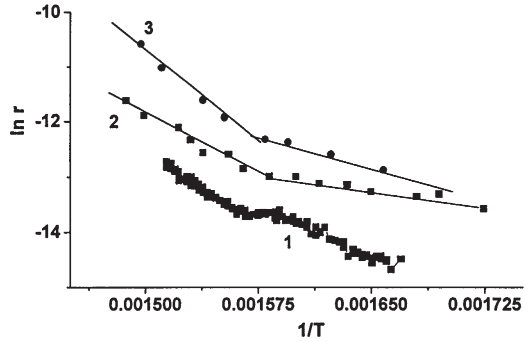

Fig. 1 Change in Arrhenius activation energy at the Curie temperature for 1 – NiO reduction with CO; 2 – catalytic CO oxidation on NiO and 3 – catalytic CO oxidation on NiO/TEG

To explain the change in mechanism of the catalytic action of Ni and NiO at a temperature near 633 K, the kinetics of the oxidation of Ni with molecular oxygen at 473–973 K and the reduction of NiO with CO at 423–703 K were studied in detail.

There are no critical phenomena at 633 K for Ni oxidation with O_2. Under non-isothermal conditions and without metallic Ni, NiO reduction with CO occurs only at >633 K. At 633±4 K, a horizontal part is observed in the $\ln r = f(1/T)$ curve (Fig. 1, curve 1). At 633 K, the mechanism of NiO reduction changes. This shows that at <633 K nuclear growth is possible. The nucleation of Ni is possible only when the temperature passes the Curie temperature of Ni. This phenomenon is connected with different states of the Ni particles [3].

On the whole, the kinetic regularities of NiO reduction with CO completely corresponded with those for catalytic CO oxidation on NiO: activation energy E_a at >633 K is more than at <633 K (Table 1).

Table 1 Activation energies (E_a) of catalytic CO oxidation and NiO reduction with CO

System	E_a (T<633 K)/kJ mol^{-1}	E_a (T>633 K)/kJ mol^{-1}
NiO+CO (reduction)	120±5	200±8
NiO+CO+O_2 (catalysis)	50±5	125±7
NiO/TEG+CO+O_2 (catalysis)	58±4	178±14

For an explanation of the mechanism of Ni-phase particle formation, the kinetic data must be compared with the TPD data [4]. The TPD data and E_a obtained from kinetic studies are shown in Fig. 2.

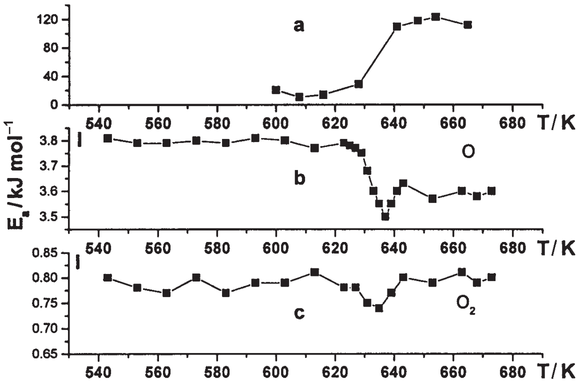

Fig. 2 Comparison of the data on oxygen desorption with E_a for catalytic CO oxidation: a – E_a *vs.* temperature; b – TPD of O from NiO surface and c – TPD of O_2 from NiO surface

The sharp decrease in O and O_2 emission from the NiO surface (Fig. 2b, c) occurs at the same temperature as the abrupt change in E_a for catalytic CO oxidation (Fig. 2a). The increase in E_a at >633 K is connected with the formation of Ni nuclei. The TPD data indicate that Ni nucleation on NiO is connected with fluctuations in oxygen density at 633 K. The mechanism of Ni fluctuation (Ni* formation) may be represented as follows:

$$NiO \leftrightarrow Ni^{*}+NiO_{1+x} \quad x>0$$

The existence of NiO_{1+x} on the NiO surface has been established by ESCA [5]. Thus, the mechanism of oxidation–reduction is possible only at >633 K. Under these conditions, the stabilization of Ni fluctuation occurs in the initial stage of the process, due to CO adsorption. The sizes of these clusters should be between 1 and 10 nm [6].

X-ray diffraction, electronic and magnetometric measurements were employed to determine the average size of the Ni particles in Ni/NiO. It is 5–12 nm when the Ni concentration is less than 5%. The sharp increase in the activation energy of catalytic CO oxidation at a temperature above 633 K is connected with the formation of these clusters. On the other hand, the number of small active surface sites increases with the catalyst dispersity [7]. It can be assumed that the number of active sites and consequently the activation energy for the NiO chemically deposited on the surface of TEG will be increased. This was observed in our experiment (Fig. 1, curve 3, and Table 1). The rate of catalytic CO oxidation on NiO/TEG and E_a are higher than those for NiO.

Conclusions

TEG is concluded to be a perspective carrier for the preparation of metal and metal oxide catalysts. The chemical deposition of NiO on TEG offers increases in the number of active surface sites and in the catalytic activity.

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