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THERMAL METHODS IN THE INVESTIGATION OF NICKEL CATALYSTS

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The thermal methods used in the investigation of nickel catalysts are summarized. These materials are nanostructured. Special attention is paid to Raney nickel and magnetic studies, especially to thermomagnetic analysis, which combined with H_2 TPD (temperature programmed desorption of hydrogen) gave valuable insight into the textural and adsorptive properties of skeletal nickel.

Keywords: *hydrogen content, nickel catalysts, thermomagnetic analysis, TPD*

Introduction

The thermal methods have been applied for long time in heterogeneous catalysis, first of all for the investigation of catalysts. These materials are nanostructured, have high surface area and their stability is limited with increasing temperature. This enables the follow-up of changes in catalyst's properties with changing temperature, like composition, particle size, phase transformations, amount of adsorbed materials. Since the basic studies of Hüttig and Selwood [1, 2] magnetic properties of the para- and ferromagnetic catalysts are measured in order to characterize the active components, like platinum, palladium or iron, nickel and cobalt. The magnetic measurements are convenient for the study of the reduction processes of the catalyst precursors [3, 4] and the characterization of the hydrogen content of the catalysts [5–7].

At the Department of Organic Chemical Technology of the Budapest University of Technology and Economics in the years 1967–1978 a magnetic balance was operated and used for the investigation of magnetic properties of industrial nickel catalysts, first of all for that of the Raney nickel [8–19]. Along with the magnetic studies thermodesorption (TPD), electrochemical and catalytic activity measurements were carried out in order to characterize the skeletal nickel catalysts in a versatile manner.

In the same period French researchers, Fouilloux *et al*. used the magnetic method together with X-ray diffraction, X-ray small angle scattering and TEM, surface determination by nitrogen adsorption and hydrogen desorption to study the texture of Raney nickel [20, 21].

Experimental

Methods

The basic method of the magnetic investigation of metal catalysts is the thermomagnetic analysis [2], according to this the magnetic susceptibility or magnetization of the sample is measured as a function of the magnetic field strength and of the temperature. For nickel catalysts, which were reduced at high temperature (>400°C), the thermomagnetic analysis up to the Curie temperature of nickel (365°C) gives the temperature dependence of the saturation magnetization and the temperature of transition to the paramagnetic state. On the basis of these data the nickel content and the so-called 'magnetic hardness' of the given sample can be determined [9].

Results and discussion

The result of the thermomagnetic analysis is the thermomagnetic curve in Fig. 1, from the saturation magnetization measured at room temperature can be calculated the metallic nickel content of the catalyst. It is 16/55.5= 0.29 namely 29 mass%. The total nickel content of the catalyst by chemical analysis was found to be 50%, so the degree of reduction is less than 60% [9].

Even more information can be gained from thermomagnetic analysis of such catalysts which are not stable in the whole temperature range of the investigation. The changes taking place during the thermal treatment can be followed by magnetization measurements. Such catalysts are the Ni for fat hardening, the Ni-boride and the Raney nickel.

In Fig. 2 the magnetization values of the lower curve represent the data during heating, the upper curve was registered during cooling. The increase of the mag-

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netization can be attributed to the structural changes of the catalyst. This means that part of the nickel was present in small crystallites which were synthered on higher temperature and became ferromagnetic. The reduction to metallic nickel can be excluded because the measurement was carried out in argon.

More pronounced was the change of magnetization of the active form of Ni-boride during thermal treatment (Fig. 3). This catalyst is prepared by the reduction of the Ni salt with $NaBH_4$. The freshly made catalyst is paramagnetic, only after the thermal treatment in argon became ferromagnetic. The temperature range of the transition of Ni-boride can be determined from the curve also, the increase of magnetization arises from the recrystallization of Ni and the desorption of hydrogen, it takes place above 200°C.

At the investigation of the skeletal Ni catalysts the thermomagnetic analysis (Fig. 4) was supplemented by TPD (temperature programmed desorption) and electrochemical polarization.

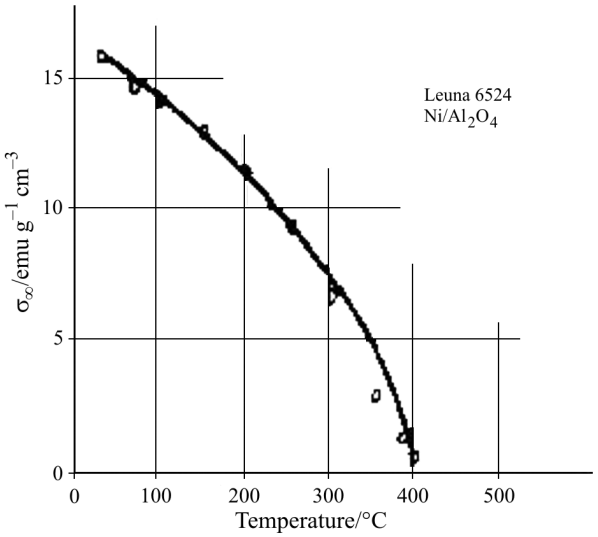

Fig. 1 Thermomagnetic curve of an alumina supported Ni catalysts [8, 9]

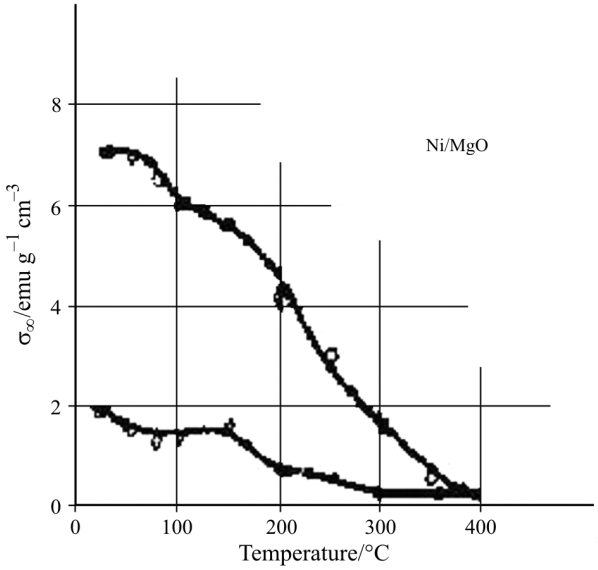

Fig. 2 Thermomagnetic curve of a magnesia supported nickel catalyst used for fat hardening [10]

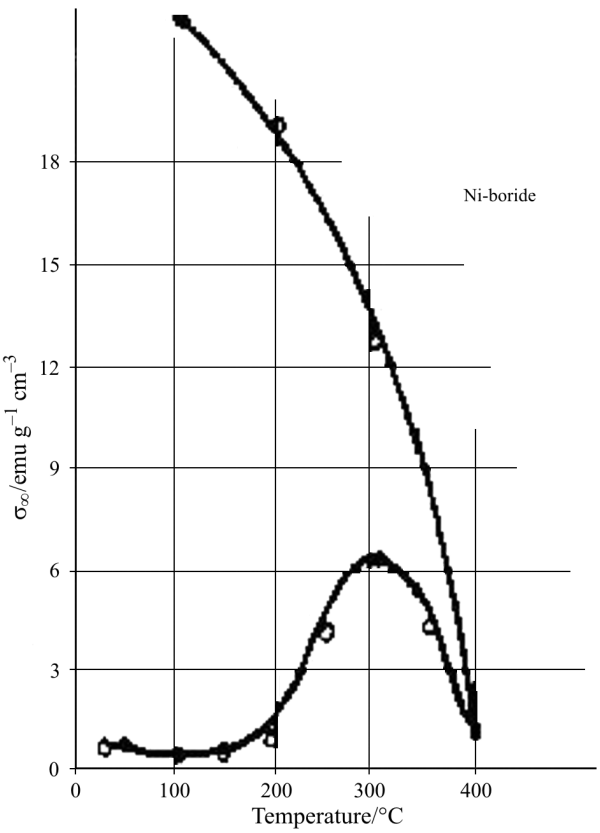

Fig. 3 Thermomagnetic curve of Ni-boride [10]

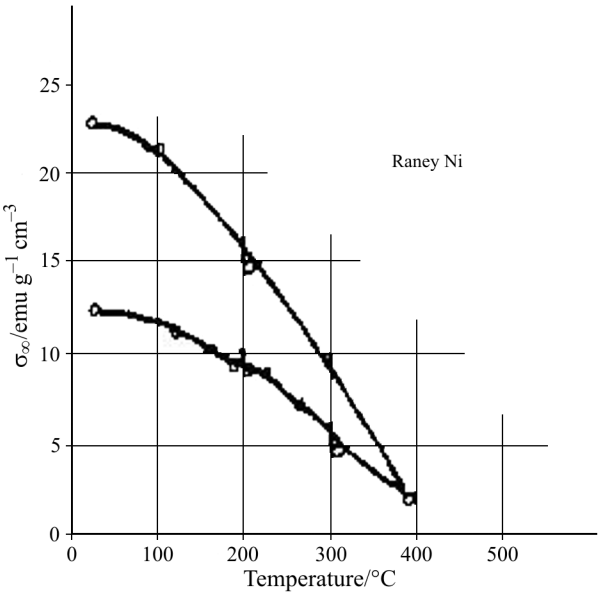

Fig. 4 Thermomagnetic curve of the Raney nickel [12]

In Fig. 5 the thermodesorptogram of the same Raney Ni catalyst in mV is plotted as a function of the temperature, which is proportional with the actual hydrogen concentration in the carrier argon gas. The Raney Ni contains two sorts of hydrogen with respect to adsorption strength, the weaker desorbs below 100°C, the stronger one desorbs between 200 and 250°C. At the thermomagnetic analysis of Raney Ni after every treatment of the catalyst at increasing temperatures a partial thermomagnetic analysis was carried out, namely the magnetization was measured at lower temperatures than the temperature of the treatment. For every treatment temperature the actual saturation magnetization and Curie temperature values were calculated on the basis of an equation valid for ferromagnetic substances [9]. The result of such measurement and calculation can be seen in Fig. 6. The saturation magnetization (σ_∞) and the Curie temperature (Θ) are illustrated as a function of the temperature of the treatment. If the increase in magnetization was attributed to the desorption of hydrogen and the change of the Curie temperature was correlated with the structural changes of the catalyst, namely with the particle size, in this case the specific magnetization change upon hydrogen desorption could be determined.

The specific value of the latter for the stronger bound hydrogen was the double of that of the weaker bound one [14]. The electrochemical polarization of the Raney Ni gave similar amount of hydrogen, this was carried out in water within the potential limits and pH values allowed on the basis of the Pourbaix diagram of the Ni. The two species could not be separated with respect to their electric charge needed for oxidation, as in liquid phase the hydrogen forms could be transformed into each other [15]. With the TPD and magnetic measurements the amount of irreversibly and reversibly adsorbed hydrogen could be determined also with measurements in argon and in hydrogen atmosphere.

The traditional thermal analysis helped the more exact characterization of the Raney Ni, the TG, DTG and DTA curves of the catalyst and the hydrargillit were compared and so could be identified the $Al(OH)_3$ content of the skeletal Ni formed during the caustic dissolution of the aluminium content of the Raney alloy [22].

At the end of the 70's our activity in this field was given up. Since that time several researchers all over the world applied among others magnetic methods for the investigation of heterogeneous catalysts, primarily for the study of Ni catalysts [23–57]. In these papers the magnetic measurements are not in the center of the research work, the data supplied by them serve as supplements to the catalytic and other physico-chemical characterization methods. Some of these magnetic methods are not thermal measurements, but concern the structure and adsorptive properties of the catalysts.

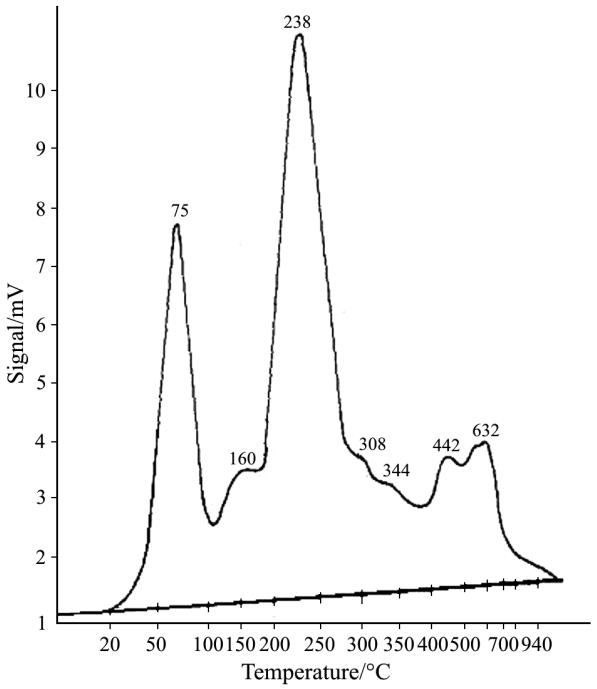

Fig. 5 TPD curve of Raney Ni [12]

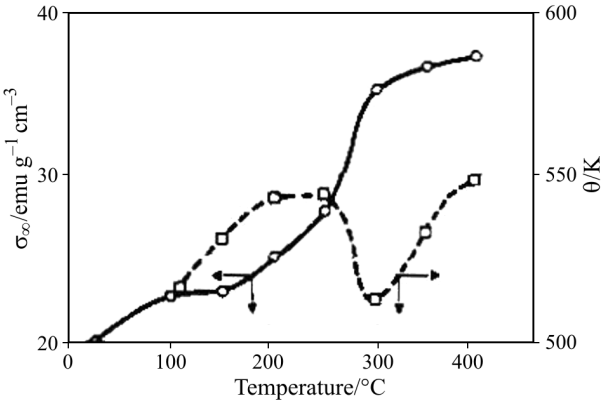

Fig. 6 The change of saturation magnetization and Curie temperature of Raney Ni as a function of the temperature of thermal treatment [14]

Conclusions

The thermomagnetic analysis turned to be a useful tool for the investigation of industrial Ni catalysts, first of all for that of the Raney Ni. Structural and adsorption properties could be determined with magnetic measurements in combination with TPD, X-ray and electrochemical methods. The skeletal Ni, the great invention of Murray Raney, can be used in a lot of industrial processes, first of all for catalytic hydrogenations. The skeletal Ni is a metastable system, which can preserve its activity, its hydrogen content only under certain conditions: covered with water or with another liquid, kept below definite tempera-

ture. The thermal methods helped a lot in the determination of the conditions among which this catalyst type could be prepared and used the best.

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