

COMPLEX STUDIES ON INDUSTRIAL NICKEL CATALYSTS

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Received July 1st, 1987

Abstract

Selected results of more than 20 year research work are summarized below. The aim has been to reveal relationships between the metal-H system, the catalysts structure and catalytic properties by using magnetic, electrochemical, TPD and X-ray measurements.

Furthermore, a new technique has been introduced for the preparation and industrial production of skeleton catalysts and a triple promoted catalyst has been developed for industrial purposes. The development work has been aided by X-ray, SIMS, electron microprobe analysis measurements.

Results and discussion

The investigation of heterogeneous metal catalysts has had long traditions at the Organic Chemical Technology Department of TUB. In the years of 1968—78 the conditions were good for research work on nickel catalysts: a thermodesorption apparatus, magnetic balance and a BET surface area determination apparatus have been built and electrochemical and catalytic activity measurements have been introduced. In cooperation with the Analytical Chemistry Department and the Applied Chemistry Department thermogravimetric, DSC and X-ray measurements were also feasible.

The aim of the work was to study structure, the hydrogen content and the activity of nickel catalysts, first of all of Raney nickel.

The thermodesorption procedure provided information about the hydrogen content of the catalyst and the hydrogen adsorption strength. The catalyst was heated with programmed rate in argon flow and the desorbed hydrogen was measured in a catalytic combustion detector.

Thermomagnetic analyses were carried out using a Faraday-type magnetic balance, whose measuring chamber could be flushed with argon and/or hydrogen and whose temperature could be varied between 20 and 450 °C. From the measured magnetization values the saturation magnetization and Curie temperature characterising the catalysts were calculated by a computing procedure according to the Weiss—Langevin formula for ferromagnetic substances [1].

In the case of Raney nickel, after changing its properties by thermal treatment a "repeated" thermomagnetic analysis was carried out, that is, after each treatment at increasing temperatures (in 50 °C steps) the magnetization was measured, at lower temperatures and the magnetization and Curie temperature characterising the catalyst in the actual state were computed [2]. Figure 1 shows a typical repeated thermomagnetic analysis curve for Raney nickel:

From the results of thermomagnetic analysis of different types of nickel catalysts the following conclusions were drawn:

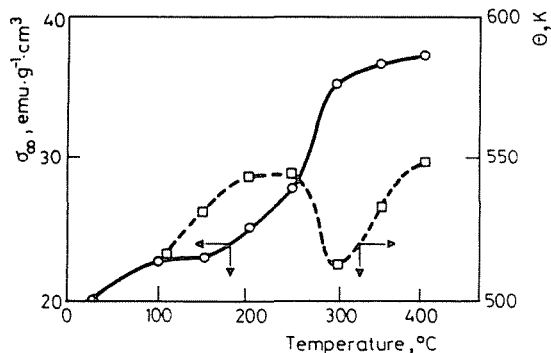


Fig. 1. Thermomagnetic analysis curve of Raney-Ni catalyst

The reduction of nickel oxide, the phenomenon of adsorption and desorption of hydrogen and the structural changes on thermal treatment could be followed [3] by the method.

The computed saturation magnetization and Curie temperature values characterize well nickel catalysts of different types.

Summarising the results of magnetic, thermodesorption, TG, DSC and electrochemical measurements we came to the following conclusions.

The major constituent of Raney-type catalysts is finely dispersed ferromagnetic nickel containing sorbed hydrogen. The Curie temperature of the catalyst is substantially ($> 80^{\circ}\text{C}$) lower than that of the bulk nickel.

The bond strengths of hydrogen desorbed at different temperatures from the catalysts are different, as demonstrated by magnetic data: the average change in magnetization is 0.1—0.3 Bohr magnetons per hydrogen atom for the weakly bound, and 0.3—0.7 Bohr magnetons per hydrogen atom for the strongly bound hydrogen. Thus, the quantity and nature of the hydrogen desorbed from the catalysts has a significant effect on the saturation magnetization of the catalyst.

A decrease of the Curie temperature occurs after heat treatment at 250—300 °C of catalysts prepared from Ni-Al alloy and at 150—200 °C of the catalyst prepared from Ni-Zn alloy. These temperature ranges coincide with the

characteristic temperature of water loss in aluminium and zinc hydroxides, and of the hydrogen desorption. From this phenomenon it is concluded that residual hydroxides have a stabilizing effect on the structure of skeleton catalysts.

Above 200°C Raney nickel undergoes a significant change, the saturation magnetization, the Curie temperature, the specific surface area and the hydrogen content (determined electrochemically and by thermodesorption) decrease and there is no catalytic activity at room temperature [4].

Correlations have been found between the quantity and quality of sorbed hydrogen, the surface area and structure of the catalysts and the catalytic activity in hydrogenation reactions at room temperature and atmospheric pressure. Thermodesorption studies show that there are two kinds, weakly and strongly bound hydrogen on the traditionally prepared Raney nickel catalysts. The quantity and nature (bond strength, characterized by the temperature of the maximum desorption rate) of sorbed hydrogen depends on the composition of the Ni-Al alloy and on the method of catalyst preparation.

The presence of other metals in the catalysts changes the quantity, forms and nature of the sorbed hydrogen. For example, a small amount of copper increases considerably the amount of strongly bound hydrogen, while the hydrogen content of the catalysts prepared from alloys containing magnesium and zinc is substantially lower than that of the one prepared from Ni-Al alloys, and there is a third type of hydrogen as well, which is desorbed at a relatively high temperature.

When a Raney nickel catalyst is dried in an inert gas flow, the adsorbed hydrogen can be removed almost completely at ambient temperature.

The magnetic and dynamic microcalorimetric measurements on dried Raney nickel catalysts samples [5] support the assumption, that the high hydrogen content of Raney nickel is stabilized by the liquid covering the catalyst (for example water) and on dry catalysts the amount of gas bound during repeated hydrogen adsorption is one order of magnitude lower but its bond strength is higher than that of skeleton Ni under water.

Using dry catalyst powders it was demonstrated that the hydrogen detected by thermodesorption up to 250°C is really a sorbed one on the catalysts and does not arise from the possible water-metal reactions which occur only at higher temperatures. The reasons for the non-pyrophoric behaviour of nickel skeleton catalysts prepared with alkali-soluble metals (Mg, Si, Zn), instead of the classical aluminium [6—9] could also be given.

In these catalysts unchanged intermetallic compounds and $\text{Me}(\text{OH})_2$, are also present, beside Me and the active nickel. The ferromagnetic nickel crystallites constitute a small part of the substance only. Both the specific surface area and hydrogen content of these catalysts are lower than those of the classical Raney nickel. The main part of hydrogen is bound more weakly than in

Raney nickel, it can be readily removed from the surface by drying in air at ambient temperature. At this low temperature the desorption is not accompanied by the oxidation of hydrogen, so the temperature of the sample does not reach the level required for the oxidation of the active nickel. For this reason the quantity of heat released at the same time is substantially smaller, therefore the processes are not self-accelerating up to a higher temperature limit.

Magnetic measurements were carried out on a Ni on alumina catalyst during benzene and cyclohexane adsorption [10]. The catalyst was reduced in hydrogen, and flushed at the same temperature (350°C) with argon, and argon-benzene or argon-cyclohexane mixtures were passed at 130° and 200°C and the decrease in magnetization was measured.

In the given temperature range over the catalyst both benzene and cyclohexane cause a significant decrease in magnetization. The effect of benzene is nearly twice as strong as that of the cyclohexane, and at 200°C the amount of irreversible bound benzene is higher, and it can be removed only at 200°C with hydrogen.

In the presence of hydrogen, cyclohexane causes practically no change in magnetization, whereas benzene has different effects depending on the partial pressure of hydrogen. This indicates that at low partial pressures the adsorption of benzene and hydrogen are competitive processes. During the catalytic hydrogenation the partial pressure of hydrogen is at least one order of magnitude higher than that of benzene, so the adsorption of benzene is less preferred (in comparison with the value measured on dehydrogenated surface it is less than 1/10).

A new method has been developed for the preparation of skeleton catalysts, the essence of which is that the alloy is decomposed in solid phase and the aluminium oxide hydrate formed partly remains in the catalyst as Ni-support. In this way metal catalysts on oxide support can also be prepared.

Fundamental research work by metal microscopy, X-ray diffraction electron, microprobe analysis, SIMS, crystallite size distribution investigations were carried out in conjunction with the development of the catalyst [11].

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