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Investigation concerning bimetallic catalysts using non-isothermal (TPR and TPD) and isothermal (pulse adsorption) methods.
Part 1. Nickel–chromium non-supported catalyst

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Abstract

The authors present some results concerning the mainly surface interaction of hydrogen with a nickel–chromium catalyst of oxidic form, based on temperature-programmed reduction (TPR), temperature-programmed desorption (TPD) and pulse adsorption data.

INTRODUCTION

Temperature-programmed reduction (TPR) is used to characterize the various forms of metallic catalysts e.g. monometallic or bimetallic supported or unsupported [1–5], zeolytes with metallic cations [6–8], etc. The technique consists of flowing a carrier gas of known hydrogen content through the catalyst bed, while its temperature increases with time, usually according to a linear heating programme. The TPR curve produced is a record of hydrogen consumption versus temperature.

Generally, a TPR spectrum can be assigned to mainly the reduction of the cations. Secondary adsorption phenomena, such as spill-over or desorption can also be detected.

Temperature-programmed desorption (TPD) consists of the previous adsorption of the investigated gas on the catalyst and a subsequent

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recording of the amount of gas desorbed as a function of temperature when the adsorbate–adsorbent system is heated according to a given programme (usually linear).

The pulse adsorption technique involves the isothermal introduction of the adsorbing gas (in this study hydrogen) in pulses and the subsequent recording of the non-adsorbed amount for every pulse.

All three techniques are sensitive to the preparation method and pretreatment conditions of the catalyst.

EXPERIMENTAL

Catalyst samples

The catalyst samples were oxidic forms of a Ni–Cr hydrogenation catalyst, with the atomic ratio of Ni:Cr being 2.3:1. The catalyst was prepared by the precipitation of a mixture consisting of basic nickel carbonate and hydrated chromium(III) oxide from a concentrated solution of nickel and chromium(III) salts treated with a concentrated solution of sodium carbonate. The mixture was subsequently washed in order to remove the sodium ions, dried at 130°C, and then calcined at 640°C. The resulting mixture contained 45.6% NiO and 20.2% Cr_2O_3, with a 34.2% weight loss on calcination in air (sample A640).

Equipment

The equipment is shown schematically in Fig. 1.

Argon and argon + 8% hydrogen flow, purified through systems A and

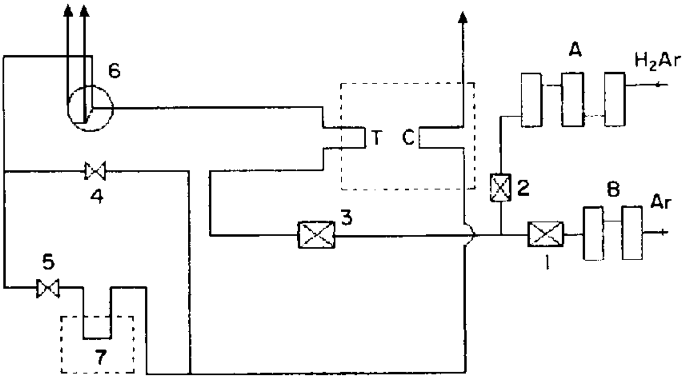

Fig. 1. Scheme of the experimental device: A, B, gas purifiers; TC, thermal conductivity detector; 1–6, valves; 7, micro-reactor.

B which consist of molecular sieves, silica gel and BTS (purifying catalyst) columns, enter the micro-reactor (7) which contains 70 mg catalyst.

The change in the hydrogen concentration of the carrier gas was recorded using a Reacrom gas chromatograph with a thermal conductivity detector(TC). In the investigated temperature range, 20–500°C, the heating rate was 9 K min^{-1}.

The gas flow was maintained at 80 $\mathrm{cm}^3\,\mathrm{min}^{-1}$.

Operating procedure

The samples had been previously submitted to a thermal treatment for two hours at 500°C in argon flow. After cooling to room temperature in argon flow, the system was switched to the gas mixture (argon + 8% hydrogen). The recorder was settled to zero and then the first-order TPR curve was recorded. The sample was then cooled down to room temperature in argon flow and the second-order TPR curve in the gaseous mixture was recorded. After cooling in argon and recording the third-order TPR curve, the sample was cooled in the gaseous mixture flow. After switching on the argon flow, the TPD curve of hydrogen to 500°C was recorded. The samples were subsequently brought to the temperature of pulse adsorption in argon flow; the temperatures chosen for pulse adsorption were 20, 100, 200, 300, and 400°C. Constant amounts of gaseous mixture (argon + 8% hydrogen) were introduced on the catalyst in 12 pulses for each temperature, and the amount of unadsorbed hydrogen which remained in the carrier gas (argon) was recorded.

RESULTS

The first- (I) and the second-order (II) curves are shown in Fig. 2. The third-order (III) TPR curve is given separately in Fig. 3 due to the change in the recorder sensivity (attenuation). The hydrogen consumption scale is 2.5 times higher for the third-order TPR curve.

As can be seen in Fig. 2, the first-order TPR curve exhibits a weak maximum located at around 230°C and a significant increase in the hydrogen consumption at 400°C. The reduction was performed at 500°C under isothermal conditions until the hydrogen consumption returned to its initial value.

The second-order TPR curve is completely different from the first-order one. Two maxima occur in the temperature range 160–200°C, followed by an increase in hydrogen consumption in the range 420–500°C. At 500°C, the hydrogen concentration is brought to its initial value, as previously shown. The hydrogen consumption corresponding to the second-order TPR curve

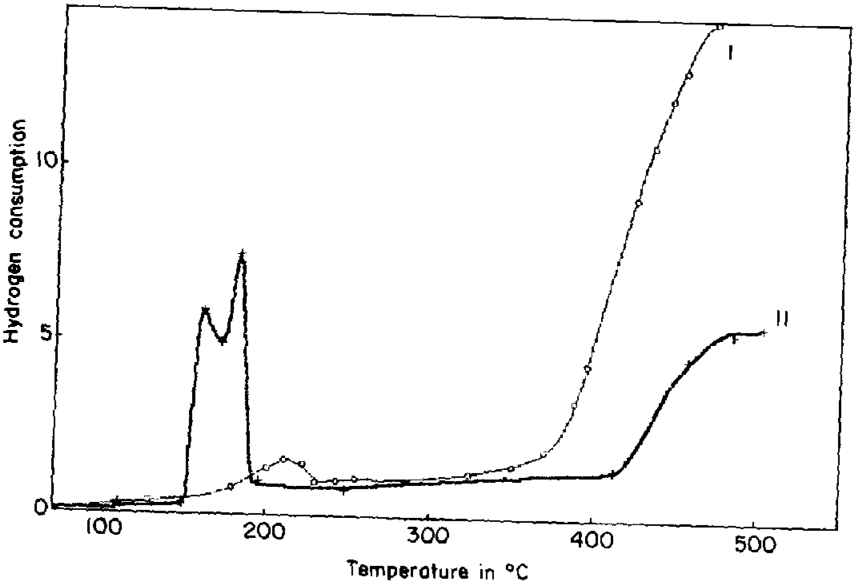

Fig. 2. First- (I) and second-order (II) TPR curves for A640 sample (attenuation 20).

is lower than for the first-order one. As shown in Fig. 3, the third-order TPR spectrum contains two distinct maxima of high hydrogen consumption in the range 170–190°C. A slow and continuous decrease in hydrogen consumption was recorded at higher temperatures (up to 400°C). No increase in hydrogen consumption above 400°C was apparent.

The TPD curve of hydrogen adsorbed on the A640 catalyst is shown in

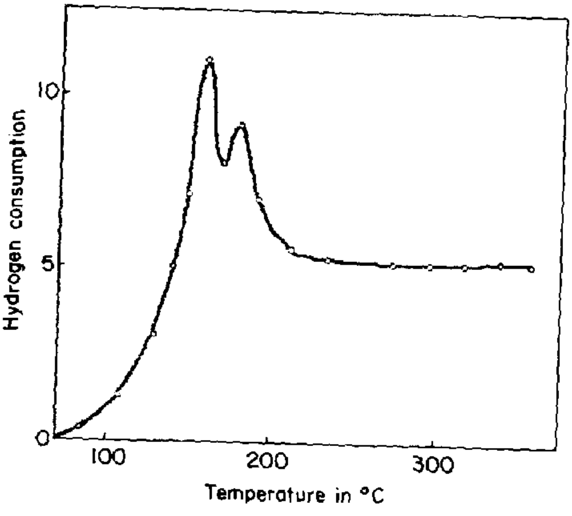

Fig. 3. Third-order curve for A640 sample (attenuation 50).

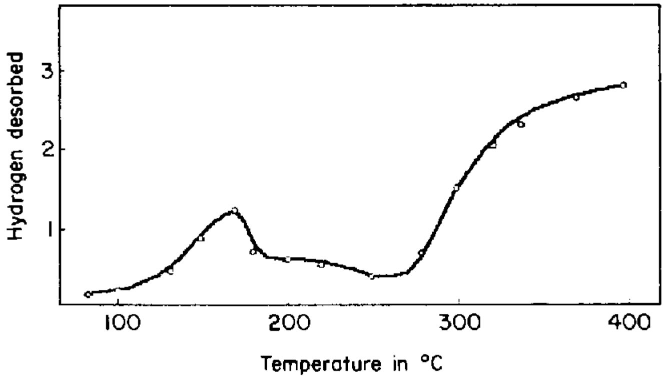

Fig. 4. The hydrogen TPD curve from A640 sample (attentuation 10).

Fig. 4. Inspection of the TPD curve shows a desorption peak at 170°C followed by an increase in the hydrogen concentration in the carrier gas above 300°C. The amount of hydrogen desorbed is lower than the corresponding amount indicated in the TPR spectra.

Figure 5 shows the data obtained in the pulse adsorption experiments. The ordinates of these curves correspond to the amount of unadsorbed hydrogen after each of the 12 adsorption pulses. Figure 5 shows that hydrogen adsorption does not occur until 200°C The retention value at 200°C is higher than at 300 and 400°C. The amount of unadsorbed hydrogen decreases when the adsorption temperature is increased.

An unexpected result was obtained for the pulse adsorption at 200°C: the first three pulses are accompanied by a decrease in unadsorbed

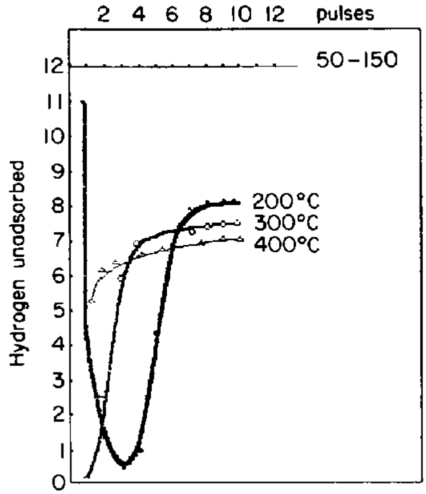

Fig. 5. Pulse adsorption curve for A640 sample (attenuation 100°C).

hydrogen concentration while the following nine pulses show a continuously increase in this concentration until it reaches a constant value.

DISCUSSION

The TPR curves of the bimetallic catalysts are not a simple superposition of the TPR curves of the individual metals [9,10]. The hydrogen consumption with increasing temperature may be assigned to: the reduction of nickel oxide to metallic nickel; the decrease in the valency of the chromium ions; and the adsorption of hydrogen on the new surface configurations.

Although the behaviour of bimetallic catalysts does not reproduce that of the individual metals, the reduction of chromium oxides below 500°C is quite improbable, although not excluded. The existence of nickel oxides and/or metallic nickel on the surface could lower the reduction temperature of chromium oxides. In such a way, surface and even bulk alloys could form.

The two maxima on the first-order TPR curve show that below 400°C, without a previous activation, hydrogen interacts only weakly with the surface. The increase in hydrogen consumption above 400°C indicates a strong interaction of the gas with the structured catalyst surface. The second-order TPR curve, with two maxima located below 200°C, shows the existence of an active surface. The maximum located at 170°C can be assigned to the adsorption of hydrogen, which has a reversible character, as shown by the peak on the TPD which appears at the same temperature. This same peak is more pronounced on the third-order TPR curve because the adsorption is taking place on a ‘more structured’ surface. The decrease in hydrogen consumption at higher temperatures can be assigned to the saturation of the surface with hydrogen and to the reduction of the oxide to metallic nickel. The TPD curve shows that the strongly adsorbed hydrogen desorbs only at high temperatures.

The second maximum which appears at 190°C in the second- and third-order TPR curves may be assigned to the change in valency of the chromium ions on the surface.

From the experimental data described, we can conclude that the TPR curves exhibit two maxima near 190°C corresponding to the change in the degree of oxidation of the chromium ions, while the other maxima located above 400°C correspond to the reduction of nickel oxide.

This interpretation is based on literature data concerning the reduction of nickel oxide in hydrogen which occurs at relatively high temperatures, above 500°C [11].

The pulse adsorption data show a quite important interaction between hydrogen and the surface at 200°C, and suggest that the activated character of the hydrogen adsorption is not present below 100°C.

CONCLUSIONS

The maxima located at 170°C on the second- and third-order TPR curves, and at the same temperature on the TPD curve can be assigned to a reversible adsorption of hydrogen. The maxima at 190°C on the second- and third-order TPR curves can be assigned to the change in valency of the surface cations.

The hydrogen consumption indicated on the TPR curves above 400°C is due to the reduction of nickel oxide and to a strong adsorption.

The hydrogen adsorption on the restructured catalyst surface exhibits an activated character.

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