Thermochimica Acta, 240 (1994) 199–205
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(94)01692-A

Investigation concerning bimetallic catalysts using nonisothermal (temperature programmed reduction (TPR) and temperature programmed desorption (TPD)) and isothermal methods. Part 2. Nickel–chromium prereduced catalysts

M. Teodorescu [a], A.C. Banciu [a], I. Sitaru [a] and E. Segal [b,*]

[a] *Institute of Physical Chemistry, Spl. Independentei 202, Bucharest, Romania*
[b] *University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, Bd. Republicii 13, Bucharest, Romania*

(Received 7 July 1993; accepted 4 January 1994)

Abstract

In a previous paper (Thermochim. Acta, 233 (1994) 317) the authors presented their results concerning TPR, TPD and pulse hydrogen adsorption on a Ni–Cr catalyst calcined at 640°C without previous reduction (sample A640). This paper deals with the influence of prereduction of the same catalyst on TPR and TPD heating cycle records (HCR) and also on pulse hydrogen adsorption even if these catalysts had been kept in air atmosphere for six months. Our results show that the influence of prereduction is preserved.

EXPERIMENTAL

The catalyst with the composition 45.6% NiO, 20.2% Cr_2O_3 and 34.2% calcination loss, obtained according to a procedure described in our previous paper [1] was partially reduced in purified hydrogen flow for 30 min at 335°C (sample A640R335) or 450°C (sample A640R450) respectively. After reduction and cooling, the catalyst was kept in air atmosphere for six months.

The equipment and operating procedures are the same as in ref. 1.

The experiments were performed with a gas mixture flow (8% hydrogen in argon) of 80 $cm^3 min^{-1}$ using argon as carrier gas which was passed through a 70 mg sample of catalyst. The changes in hydrogen concentration were followed using a thermal conductivity cell. The experimental system has been shown in our previous paper [1].

The temperature was automatically controlled and programmed in the range 20–500°C with a heating rate of 9°C min^{-1}.

* Corresponding author.

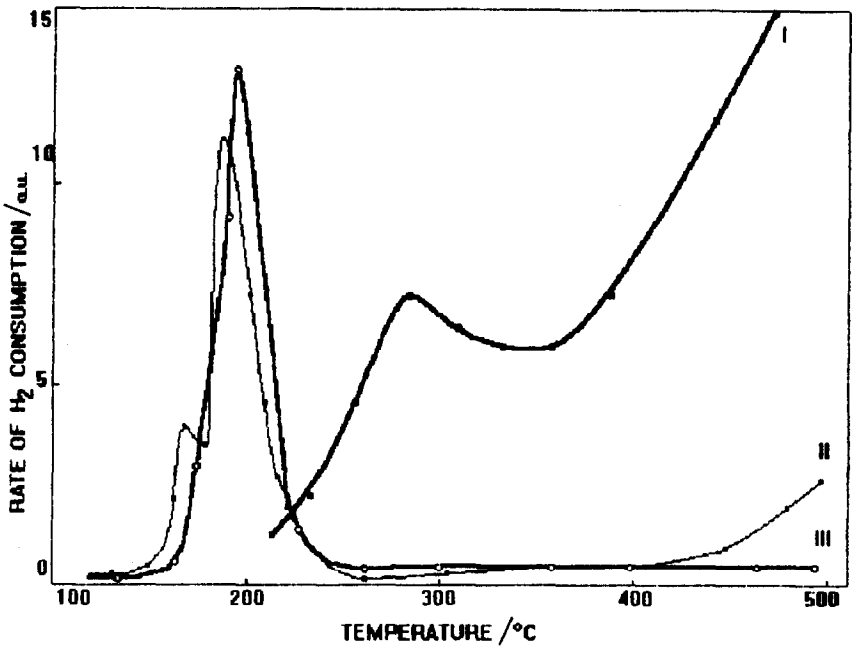

Fig. 1. First, second and third order TPR curves of sample A640R335 (arbitrary units).

The TPR curves of first, second and third order have been recorded after cooling the samples in argon. Actually the rate of hydrogen consumption versus temperature gives the TPR curve.

The TPD HCR were obtained after cooling the sample in a flowing mixture of 8% hydrogen in argon in order to adsorb hydrogen. The TPD curves (hydrogen evolved versus temperature) were recorded by using argon as carrier gas.

The pulse adsorption experiments were performed after cooling the samples in argon in order to remove traces of preadsorbed hydrogen. Using argon as carrier gas, the amount of unadsorbed hydrogen was recorded for each of the 12 introduced pulses.

RESULTS

Sample A640R335

The first, second and third order HCR are given in Fig. 1. Notice the higher hydrogen consumption revealed by the first order HCR. This curve exhibits only one peak located at 280°C followed by an important increase of hydrogen consumption at temperatures higher than 400°C. The second order HCR exhibits two peaks in the temperature range 180–200°C followed by a lower increase of hydrogen consumption at higher temperatures. The third order HCR exhibits only one peak located at 200°C with no hydrogen consumption at higher temperatures.

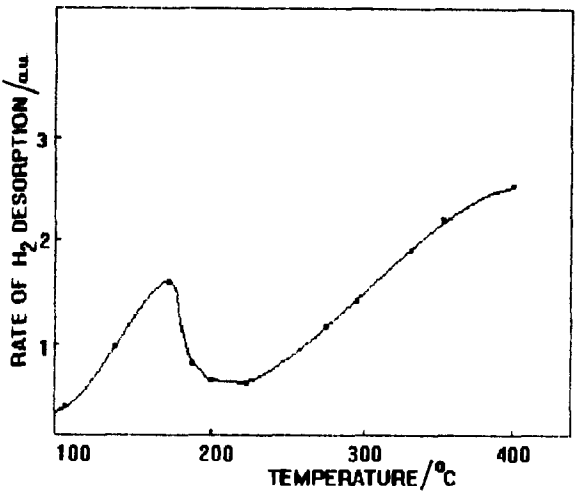

Fig. 2. TPD curves of sample A640R335.

The TPD curve shown in Fig. 2 exhibits a peak located at about 180°C followed by a continuous increase of hydrogen desorption at higher temperatures.

The pulse adsorption curves are given in Fig. 3. The decrease of hydrogen adsorption with temperature should be noted. At temperatures lower than 180°C hydrogen adsorption was not observed.

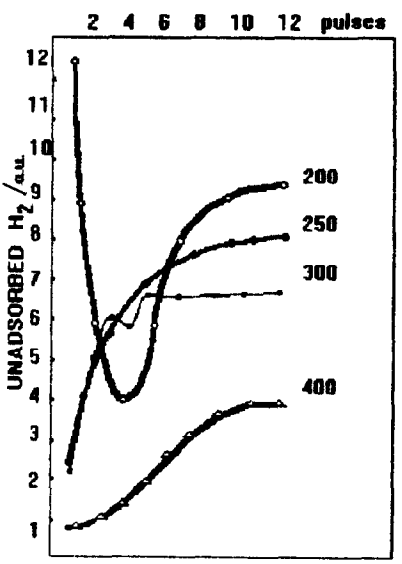

Fig. 3. Hydrogen pulse adsorption curves for various temperatures (sample A640R335).

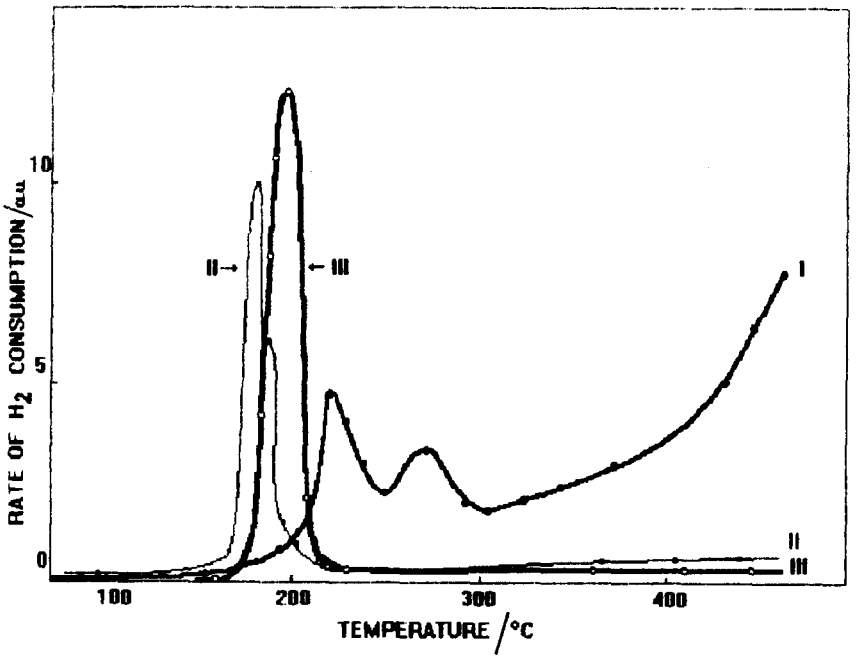

Fig. 4. First, second and third order TPR curves of sample A640R450.

Sample A640R450

The first, second and third order HCR are given in Fig. 4. Inspection of the figure shows two peaks located at 220°C and 280°C for the first order HCR, followed by an increase of hydrogen consumption at higher temperatures. The second order curve exhibits two peaks shifted toward lower temperatures (at 180°C and 200°C), with almost no hydrogen consumption at higher temperatures. The third order HCR exhibits only one peak located around 200°C.

The TPD curve and the pulse adsorption curves are quite similar to the corresponding curves for sample A640R335.

In order to obtain a general picture for the results, the first, second and third order TPR HCR for samples A640R335 and A640R450 are given in Figs. 5–7.

In Fig. 5 one can notice one or two peaks at lower temperatures and the high hydrogen consumption at high temperatures. Actually only the most reduced sample (A640R450) exhibits two peaks. The second order curve (Fig. 6) exhibits two peaks at lower temperatures followed by low hydrogen consumption or no hydrogen consumption at higher temperatures. On the third order curve (Fig. 7) there is only one peak at low temperatures and no hydrogen consumption at high temperatures.

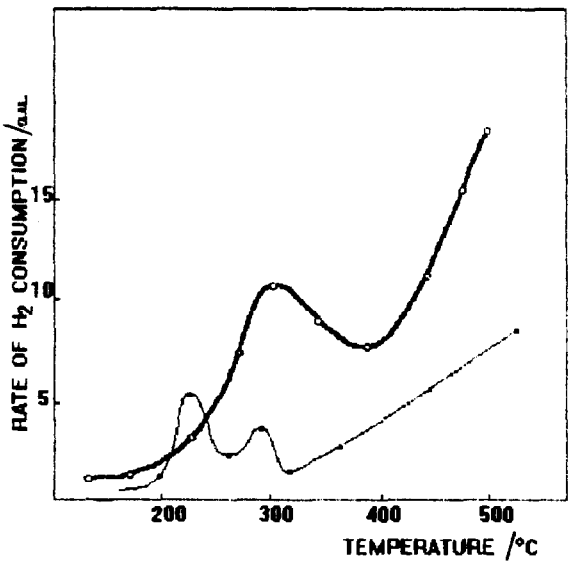

Fig. 5. First order TPR curves of samples A640R335 (○) and A640R450 (■).

DISCUSSION

Considering the behaviour of samples A640R335 and A640 described in ref. 1 one notices that although they were kept in air atmosphere, the TPR data are different for those initially reduced and those initially unreduced.

The first order TPR curve of sample A640 (Fig. 2 of ref. 1) shows only one maximum while sample A640R450 exhibits two maxima. For all three

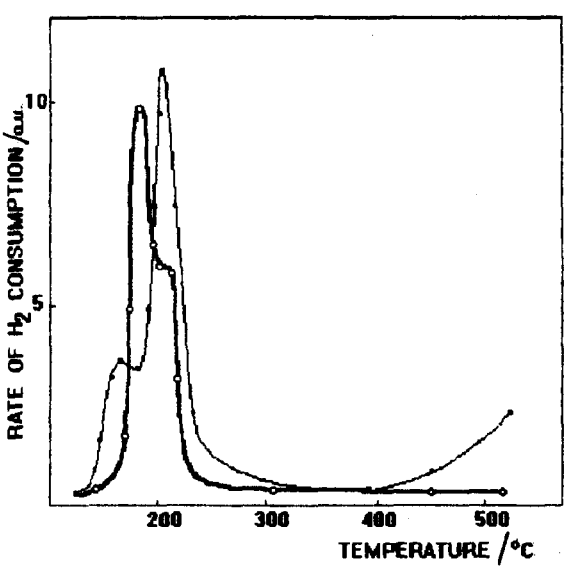

Fig. 6. Second order TPR curves of samples A640R335 (■) and A640R450 (○).

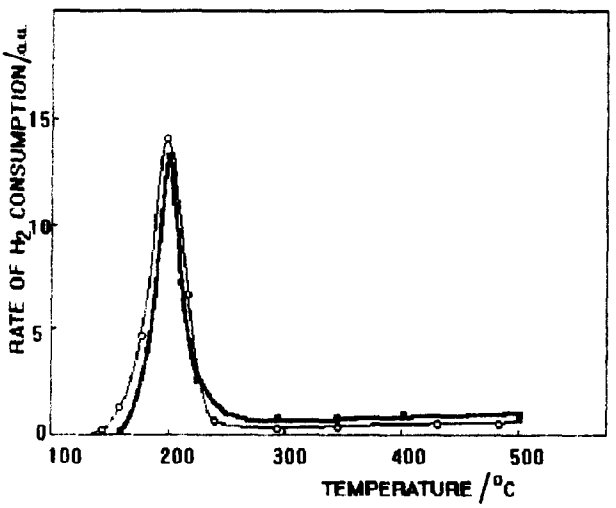

Fig. 7. Third order TPR curves of samples A640R335 (■) and A640R450 (○).

samples one can notice high hydrogen consumptions at high temperatures. These hydrogen consumptions decrease with the initial degree of reduction.

The second order TPR curve exhibits two maxima for sample A640 (Fig. 2 of ref. 1) and also for samples A640R335 and A640R450 (Fig. 6). The hydrogen consumption at high temperatures is lower than for the first order TPR curve and again decreases with the degree of reduction (sample A640R450 does not exhibit hydrogen consumption at all).

The third order curve for sample A640 (Fig. 3 of ref. 1) exhibits two more maxima at lower temperatures while samples A640R335 and A640R450 (Fig. 7) exhibit only one. At high temperatures the last two samples do not exhibit hydrogen consumption whereas at high temperatures the first sample exhibits a constant but still important hydrogen consumption.

In agreement with previous works [2–5], taking into account that NiO can be reduced at temperatures higher than 500°C and Cr_2O_3 at still higher temperatures and that generally properties of alloys do not result through superposition of properties of the constituent metals, the conclusions from ref. 1 are still valid.

The hydrogen consumption recorded in the TPR measurements could be assigned to reduction of the surface oxides, adsorption of hydrogen on the metals generated through reduction and hydrogen spillover.

Analysis of the results permits the qualitative estimation of the degree of surface reduction from the numbers and form of the TPR peaks. Thus one can distinguish the following:

(i) a weakly reduced surface, characterized by only one peak at low temperatures with low intensity and high hydrogen consumption at higher temperatures;

(ii) a moderately reduced surface, characterized by two sharp peaks at low temperatures and low hydrogen consumption at high temperatures;

(iii) a strongly reduced surface, characterized by only one peak at low temperatures and no hydrogen consumption at high temperatures.

The behaviour of the two samples investigated in this work also shows that the initial prereduction influences the samples even after keeping them in air atmosphere for long periods. The second order TPR curve of sample A640R450 (Fig. 5) exhibits two maxima, similar to the second order TPR curve of the initially unreduced sample A640 (Fig. 2 of ref. 1) and sample A640R335 initially submitted to a weak reduction (Fig. 6), while the third order TPR curve of sample A640 (Fig. 3 of ref. 1) exhibits two maxima as do the second order TPR curves of samples A640R335 and A640R450 (Fig. 6).

The maximum shown by the pulse adsorption of hydrogen curve at 200°C could be attributed to the fact that adsorption requires a previous reduction which is accomplished by adsorption during the first three pulses.

ACKNOWLEDGEMENTS

The authors are indebted to G. Dobrescu and V. Chihaia for information processing.

REFERENCES

1 M. Teodorescu, A.C. Banciu, I. Sitaru and E. Segal, Thermochim. Acta, 233 (1994) 317.
2 A. Jones and B.D. McNicol, Temperature Programmed Reduction for Solid Materials Characterisation, Dekker, New York, 1986.
3 Y.J. Huang, J. Xue and J.A. Schwarz, J. Catal., 11 (1988) 59.
4 J.L. Falconer and J.A. Schwarz, Catal. Rev., 25 (1983) 141.
5 J.A. Schwarz and J.L. Falconer, Catal. Today, 7 (1990) 1.