

Morphology of Nickel/Alumina Catalysts

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Received January 14, 1981; revised October 14, 1981

The morphology of impregnated nickel/alumina catalysts before and after the reduction process was studied. The temperature-programmed reduction method was successfully utilized for the study of the catalyst prior to the reduction. Nickel oxide was found to appear in the catalysts in two forms, as "free" or "fixed" oxide. The occurrence of the fixed form of the oxide in the catalysts is connected with the formation of nickel aluminate. As a result of the reduction of free and fixed forms of nickel oxide, respectively, large and small nickel crystallites are produced and a bidispersed structure consequently develops in the catalysts. Small and large nickel oxide crystallites are found to undergo reduction with the same ease. The difficult reduction of supported catalysts which is observed is due to chemical interaction of nickel oxide with the support.

INTRODUCTION

The last stage in the preparation of Ni/Al₂O₃ catalysts is a reduction process. The morphology of the catalyst and its associated catalytic properties depend on the manner in which the reduction process is carried out. The reduction of NiO/Al₂O₃ and the effect of the reduction conditions on the catalytic properties of the resulting Ni/Al₂O₃ have been the subject of numerous studies (1-6). It is much more difficult to reduce NiO/Al₂O₃ than nickel oxide powder. This fact is generally ascribed to the interaction of nickel oxide with the support. Another concept assumes that small nickel oxide crystallites which occur on supported catalysts undergo reduction with less ease than large crystallites of nickel oxide powder (7, 8). Physical studies of the NiO/Al₂O₃ system have shown that nickel oxide can react with alumina to give stoichiometric or nonstoichiometric nickel aluminate (9, 10). The amount of the aluminate formed and its structure depend on the conditions of preparation of the catalyst. The aluminate may occur in the catalyst in an amorphous or crystalline form.

This paper is concerned with a study of the effect of the morphology of NiO/ γ -

Al₂O₃ catalysts on the morphology of the Ni/ γ -Al₂O₃ catalysts obtained by reduction and is a part of a wider research of nickel/alumina catalysts and their catalytic activity in the hydrogenation of CO and CO₂. The morphology of the NiO/ γ -Al₂O₃ catalysts was investigated largely by following the reduction process itself in the belief that nickel oxide and nickel aluminate present in the catalyst should behave in a different manner in the hydrogen reduction reaction. Hence, their presence could be detected with also a possible determination of their respective quantities. The reduction measurements were carried out with a linearly programmed temperature rise. Robertson *et al.* (11) have used temperature-programmed reduction (TPR) for investigation of (Cu,Ni)/SiO₂ bimetallic catalysts. They found copper oxide and nickel oxide to interact with silica. In the reduced catalysts a Cu-Ni alloy was formed.

In this study the surface area and the amount of nickel were determined from the measurement of oxygen sorption after TPR of NiO/ γ -Al₂O₃ without removing the samples from the apparatus. In some catalysts the nickel crystallite size distribution was separately measured by small angle X-ray scattering.

EXPERIMENTAL

Apparatus. The TPR studies of NiO/ γ -Al₂O₃ and the measurements of the surface and quantity of the metal in the catalysts after reduction were carried out in a flow system. The reduction rate was estimated from the hydrogen consumption in a stream of hydrogen-argon mixture. The surface area and the amount of nickel in the reduced catalysts were determined by measuring the sorption of oxygen pulses admitted into a helium stream.

A schematic diagram of the all-glass apparatus is shown in Fig. 1. Hydrogen, argon, and helium were of 99.99% purity. The hydrogen-argon mixture (75% H₂) and helium were purified in successive columns packed with Cu/SiO₂, silica gel, and molecular sieve 5 A. Hydrogen was purified by a palladium filter. The gas stream required was fed to the measuring system by means of a four-way valve and passed through a column packed with copper metal powder heated to 100°C, a cold trap cooled with dry ice, and a reference thermal conductivity cell. By means of three four-way stopcocks

it was possible to switch in or out a saturator, a microreactor, and a cold trap. The thermostatted saturator filled with water was used in a study of the effect of water vapor on the reduction rate, and in the cold trap the gas stream leaving the reactor was dried before it was allowed into the thermal conductivity cell.

A glass gradientless microreactor was used or, when necessary because of a high temperature of the measurement, a U-tube quartz reactor. The reactor was heated by a fast-response resistance furnace. A temperature control system maintained the reactor temperature to within 1°C over the range of -200 to 800°C and provided a linear temperature programming.

Materials. NiO/ γ -Al₂O₃ was obtained by impregnation of γ -alumina (surface area 111 m² g⁻¹ and grain size 0.15–0.35 mm) with an aqueous nickel nitrate solution. The alumina, prepared by hydrolysis of aluminum isopropoxide, was calcined for 12 h at 700°C prior to the impregnation. The stirred suspension was evaporated to dryness under an infrared lamp. The material was dried at 105°C, then calcined in a helium

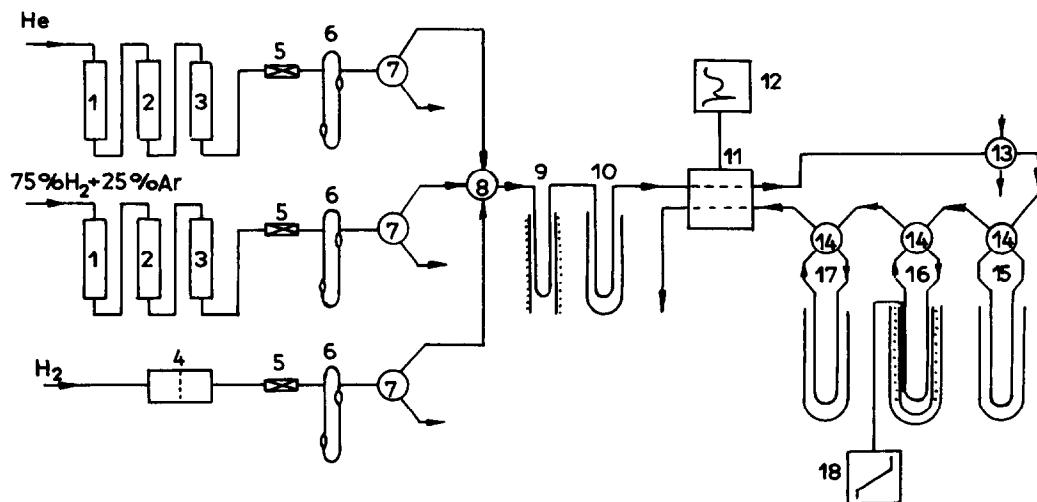


FIG. 1. Diagram of the apparatus: 1, column packed with Cu/SiO₂ catalyst; 2, silica-gel column; 3, molecular sieve 5A column; 4, palladium filter; 5, needle valve; 6, flowmeter; 7, three-way valve; 8, four-way valve; 9, copper powder column; 10, dry-ice cold trap; 11, thermal conductivity cell; 12, recorder; 13, sampling valve; 14, four-way valve; 15, saturator; 16, microreactor; 17, dry-ice cold trap; 18, temperature controller and recorder.

stream under a linearly increasing temperature (0.7°C/min) from room temperature to 400°C, at which temperature it was calcined for another hour. By the manner described a series of NiO/Al₂O₃ preparations with nickel concentrations in the reduced form of 2, 5, 10, 20 and 40 wt% were obtained.

Nickel oxide was prepared by thermal decomposition of nickel nitrate. Calcination was performed analogously as for supported catalysts. Investigation of the composition of the gaseous reduction products showed that both the nickel oxide and the NiO/ γ -Al₂O₃ contained no undecomposed nickel nitrate.

Method of measurement. Typically 25-mg samples of the NiO/ γ -Al₂O₃ were used. Prior to the reduction the sample was dried for a half hour in a helium stream (40 cm³/min) at 400°C. On cooling the sample to room temperature helium was replaced by the hydrogen-argon mixture, then the reactor temperature was linearly raised and the hydrogen concentration change in the H₂-Ar mixture was measured. The H₂-Ar mixture flow rate was 20 cm³/min, and the rate of temperature rise was 8.3°C/min. When the required temperature was attained the catalyst was reduced for another 30 min. From the sample thus reduced hydrogen was desorbed in a helium stream (40 cm³/min, 400°C, 0.5 h) and then oxygen was adsorbed on the catalyst by admitting 39- μ l oxygen pulses into the helium stream. Adsorption measurements at 0°C were made to determine the metal surface area assuming that 1.7 atom of adsorbed oxygen occurs per one surface nickel atom (12). From the measurements of oxygen sorption at 400°C the amount of nickel in the reduced catalyst was determined on the assumption that NiO is formed during the oxidation (5).

RESULTS AND DISCUSSION

The reduction rate of supported catalysts depends on a number of factors of chemical and structural nature. This may cause problems in the interpretation of the results ob-

tained by the TPR method and make it necessary to supplement these measurements with other studies.

At room temperature at which the TPR measurements were started hydrogen does not react with NiO/ γ -Al₂O₃. As the temperature is raised the peaks characteristic of hydrogen consumption are first observed and, with a minor delay, water appears in the gaseous phase.

Figure 2 shows the TPR curves for nickel oxide and the NiO/ γ -Al₂O₃ series. The TPR curve for pure nickel oxide powder has a single peak of hydrogen consumption with a maximum at 230°C. For the supported catalysts of high nickel concentration two hydrogen consumption peaks appear on the TPR curves. The first, low-temperature, peak shows up at much the same temperature as for pure nickel oxide; the other, very broad, has a maximum at 450°C. For supported catalysts of low nickel concentration only the high-temperature peak of hydrogen consumption is observed.

The appearance of a TPR peak for supported catalysts at the same temperature as for pure nickel oxide appears to indicate that in the catalysts of that type pure nickel oxide is present. This oxide will be referred

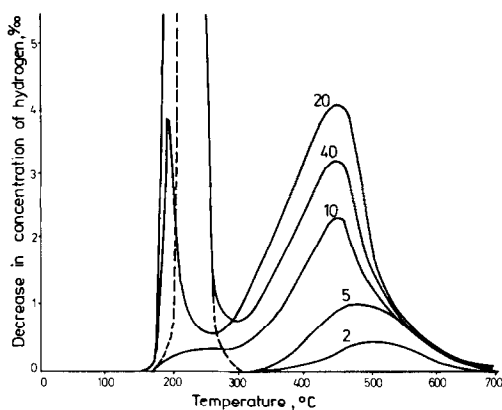


FIG. 2. Temperature-programmed reduction of NiO powder and NiO/ γ -Al₂O₃. Sample weight, 25 mg; flow rate of H₂-Ar mixture, 20 cm³/min; heating rate of temperature rise, 8.3°C/min; ---, NiO; —, NiO/ γ -Al₂O₃. Numbers by the curves denote nickel concentration in the solids.

to as "free" nickel oxide. It is at the same time assumed that the high-temperature hydrogen consumption peak on the TPR curves is due to the reduction of the nickel oxide which has interacted with alumina and this oxide will henceforward be referred to as "fixed" nickel oxide. The occurrence of fixed nickel oxide in supported catalysts is related to a chemical reaction forming stoichiometric or nonstoichiometric nickel aluminate. Evidence to support this concept will be provided in the subsequent part of this paper.

Figure 3 shows a schematic diagram of the structure of the nickel alumina catalyst prior to and after the reduction. The nickel oxide that remains in direct contact with the gaseous phase (reduction mixture) is the

free nickel oxide. Its reduction occurs at the same temperature as that of pure unsupported nickel oxide. The nickel oxide in the nickel aluminate form, in fact no longer nickel oxide, or as a solid covered by a tight nickel aluminate layer is the fixed nickel oxide. Its reduction occurs at a higher temperature than that of free nickel oxide. Additionally in Fig. 3 is marked the nickel oxide that is recorded in the measurements by X-ray phase analysis.

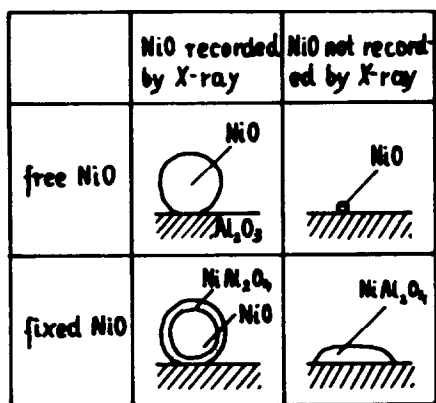
The fraction of fixed nickel oxide present in the $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ depends on the preparative procedure used. It was found from measurements not reported in this paper that this fraction is larger for impregnation of alumina with nickel ammonia complex than with nickel nitrate, is larger for $\gamma\text{-Al}_2\text{O}_3$ than for $\alpha\text{-Al}_2\text{O}_3$, and increases with temperature and calcination time.

Comparative TPR measurements in which the weight of the $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ sample or the $\text{H}_2\text{-Ar}$ mixture flow rate was varied demonstrated that the water vapor produced from the reaction has virtually no effect on the temperature-programmed reduction. The use in the TPR measurements of an $\text{H}_2\text{-Ar}$ mixture saturated with water vapor at 0°C makes the reduction peaks of the free and fixed oxides shift toward higher temperatures by 60 and 30°C , respectively, but the area of the peaks remains unaltered. This appears to suggest that the TPR measurements can be used for determination of the amount of nickel oxide in its free and fixed forms and thus can be used for identification of the $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalysts.

X-Ray evidence demonstrates that the alumina used consists of the poorly crystallized γ -form. In the $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ samples the $\gamma\text{-Al}_2\text{O}_3$ peaks decrease with a nickel content in the sample which is indicative that alumina has reacted with NiO . The X-ray data, however, have not given convincing support of the formation of nickel aluminate, as suggested by Lo Jacono *et al.* (9), because it was very poorly crystallized on account of the low calcination temperature.

The relation of the amounts of the var-

a Before reduction



b After reduction

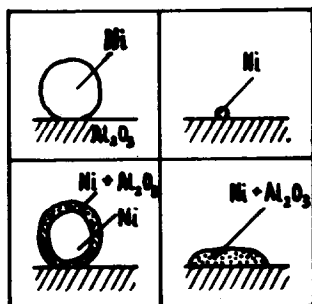


FIG. 3. Model of the nickel-alumina structure before and after the reduction.

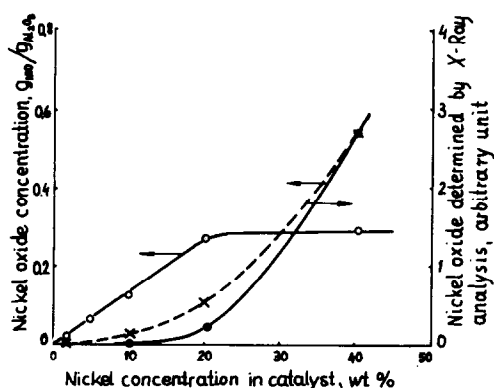


FIG. 4. Concentration of various nickel oxide forms vs nickel concentration in the NiO/ γ -Al₂O₃ samples: ○, fixed NiO; ●, free NiO; ×, NiO detected by X-rays.

ious forms of nickel oxide in the NiO/ γ -Al₂O₃ samples to the nickel concentration is shown in Fig. 4. Results obtained from the TPR measurements are denoted with a solid line. The broken line shows the amount of nickel oxide, in arbitrary units, as determined from the X-ray phase analysis. The results were calculated from the surface area of NiO peaks taking a mean value for the (111), (200), and (220) peaks. With increasing nickel content the amount of fixed nickel oxide increases linearly to a certain limiting level. Approximately from that point free nickel oxide appears. The relation of the free nickel oxide content obtained from the TPR measurements roughly agrees with the results obtained by X-ray phase analysis. It should be noted, however, that the amounts of nickel oxide determined by the respective methods are different. This is due to the fact that the fine crystallites of pure nickel oxide are not recorded in the X-ray studies, but they are determined in the TPR measurements; on the other hand, large crystallites of pure nickel oxide covered by a tight nickel aluminate layer will be seen by X-rays as nickel oxide, whereas in the TPR measurements they will become reduced as fixed nickel oxide. The coincidence of the TPR and X-ray data suggests that the free NiO occurs in the samples primarily as large-

size crystallites (small-size crystallites have reacted with alumina during the calcination process) and that the fixed nickel oxide is present largely as nickel aluminate.

On the basis of the TPR results shown in Fig. 4 the average thickness of the nickel aluminate layer in the NiO/ γ -Al₂O₃ samples was determined. An assumption was made in the calculations, which is inconsistent with the model presented in Fig. 3, that fixed nickel oxide occurs in the form of a uniform layer of the stoichiometric nickel aluminate only on the alumina surface. The sought thickness of the layer in a sample of a concentration of 40% Ni is 1.4 nm. The corresponding value for a sample of 20% Ni content is 1.3 nm, and in samples of a still lower concentration is proportionally lower.

The model of the structure of NiO/ γ -Al₂O₃ outlined above in conjunction with the TPR data can elucidate the properties of these solids after reduction. Figure 5 shows for a 20% Ni/ γ -Al₂O₃ catalyst the relation of the degree of reduction, nickel surface area, and average metal crystallite size calculated from the surface as a function of the temperature at which the temperature-programmed reduction was terminated. During the temperature-programmed reduction the free nickel oxide reacts first. The surface

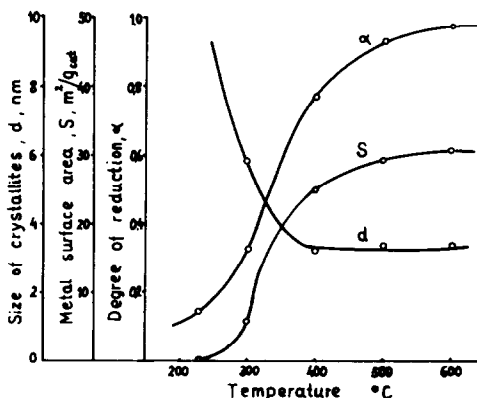


FIG. 5. Degree of reduction, specific surface area of the metal (per gram of the reduced catalyst) and crystallite size vs the reduction temperature for the 20% Ni/ γ -Al₂O₃ catalyst.

area of the metal formed is very small and the crystallites are very large. At about the completion of reduction of free nickel oxide the fixed nickel oxide begins to react. As a result of the reduction of nickel aluminate small nickel crystallites appear in a huge amount so that the metal surface area in the catalyst increases considerably and the average crystallite size diminishes.

As a result of nickel aluminate reduction besides fine nickel crystallites also alumina is formed. Upon reduction this is likely to remain in the close vicinity of the metal (Fig. 3b). This fact may have a vital effect on the catalytic properties of nickel.

Figure 6 shows the relation of the degree of reduction, surface area, and the average size of metal crystallites with nickel concentration for the Ni/ γ -Al₂O₃ catalyst series studied. With increasing nickel concentration the degree of reduction gradually grows and the metal surface area initially becomes higher to attain a maximum at a concentration of 20 wt% Ni, and thereafter to decline. Comparison with the TPR results in Fig. 4 indicates that a maximum metal surface area is obtained when the fixed nickel oxide concentration attains a limiting value and the free nickel oxide concentration is low. The average size of nickel

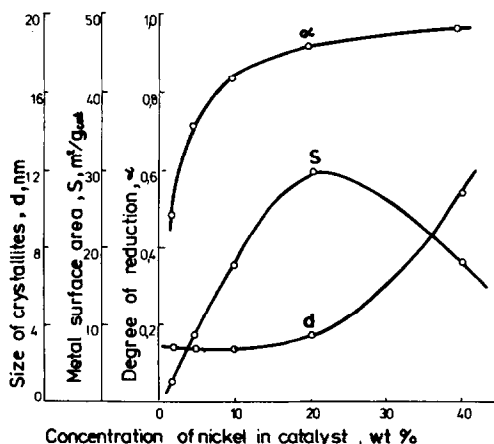


FIG. 6. Degree of reduction, specific surface area of the metal (per gram of the reduced catalyst) and crystallite size vs nickel concentration in the catalysts. Catalyst reduction temperature 500°C.

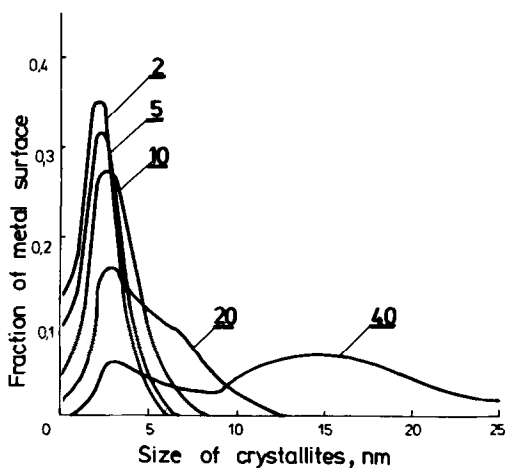


FIG. 7. Nickel crystallite size distribution in the Ni/ γ -Al₂O₃ catalyst. The numbers by the curves refer to the metal concentration. Catalyst reduction temperature 500°C.

crystallites calculated from the metal surface area is roughly constant for the catalysts of a concentration lower than 20% and increases above that value with the rise in the content of free nickel oxide.

The model of the structure and reduction of the NiO/ γ -Al₂O₃ preparations advanced here has been substantiated by results on the nickel crystallite size distribution in the reduced catalyst (Fig. 7). The measurements were made by the small angle X-ray scattering method, filling the pores of the catalyst with methylene iodide of electron density equivalent to the support. The catalysts of low nickel concentration in which nickel oxide occurred merely as its fixed form have only small size crystallites, whereas the catalysts which had both forms of nickel oxide are bidisperse. These results give support to the previous suggestions as to the mechanism of formation of bidisperse structure of the Ni/ γ -Al₂O₃ catalysts (3, 13).

Oxygen sorption of 400°C on the Ni/Al₂O₃ catalysts leads to a complete nickel oxidation to stoichiometric NiO (5). Figure 8 shows a TPR curve for the 2% Ni/ γ -Al₂O₃ catalyst first reduced at 500°C then oxidized at 400°C. Reduction occurs largely at the

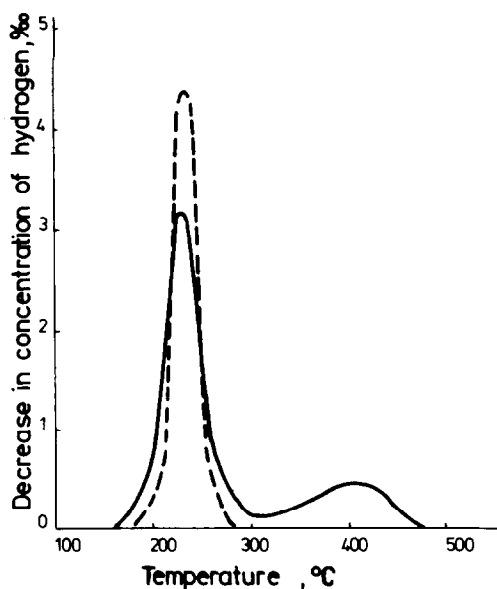


FIG. 8. TPR curves for NiO powder (---) and for 2% Ni/ γ -Al₂O₃ catalyst first reduced then oxidized at 400°C (—). NiO sample weight, 1 mg; 2% Ni/ γ -Al₂O₃ sample weight, 100 mg; flow rate of H₂-Ar mixture, 20 cm³/min; heating rate, 8.3°C/min.

same temperature as that of pure unsupported nickel oxide indicating that in this solid it is the free nickel oxide that prevails, rather than the bonded NiO as was the case of the condition preceding the first reduction (Fig. 2).

Cyclic oxidation at 400°C alternating with temperature-programmed reduction of the 2% NiO/ γ -Al₂O₃ has no effect on the metal surface area or the shape of the TPR curves. Since the distance between the nickel crystallites in the catalyst is fairly large (nickel crystallites occupy about 0.4% of the area of alumina) it can be believed that in successive oxidations followed by reduction from one nickel crystallite one nickel oxide crystallite is formed, and conversely, in other words, the sizes of nickel oxide crystallites are similar to those of nickel crystallites (cf. Figs. 6 and 7). The reduction of the fine nickel oxide crystallites under consideration in the TPR measurements occurs at just the same tempera-

ture as that of large crystallites of nickel oxide powder. This indicates that the difficult reduction of the NiO/ γ -Al₂O₃ samples observed is not due to dispersion of nickel oxide but results from the presence of nickel aluminate formed during the catalyst preparation, which undergoes reduction with much more difficulty than pure nickel oxide.

ACKNOWLEDGMENTS

This work was carried out with Research Project 03.10. The author wishes to thank Dr. J. Pielaszek for his X-ray studies of the catalysts and Dr. R. Frał for measurements of distribution of the crystallites. Special thanks are acknowledged to Professor W. Palczewska for valuable suggestions during the preparation of the paper.

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