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INVESTIGATION OF CHANGES IN CATALYST FOR CONVERSION BY MEANS OF STEAM DURING USE IN AN INDUSTRIAL REACTOR

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A study was made of the changes in the active component of a commercial catalyst for methane reforming by means of steam, as a function of its duration of use and of its position in an industrial reactor. The samples for examination were taken after 3, 8, 9 and 20 months of catalyst use, and from seven different levels in the reformer tube, ranging from the top to the bottom.

DTA, TG, IR spectroscopy, X-ray diffraction and surface area determination were used to follow the catalyst changes.

For methane reforming by means of steam, in the first stage of ammonia production from natural gas, metallic nickel on a support with a developed surface is used as catalyst. At the moment of delivery, the active component of the catalyst, is in the form of nickel oxide, which is promoted to the active form by reduction in the industrial reactor. The literature contains data on examinations of model catalyst systems involving nickel on alumina as support, but there are no data about the behavior of commercial catalysts in industrial reactors, which could be useful for the explanation of the aging and deactivation process.

Our examinations related to the changes in the active component of a commercial catalyst for methane reforming with steam, as a function of the duration of its use and its position in an industrial reactor. Differential thermal and thermogravimetric analysis were used to follow these changes, and some samples were subjected to IR spectroscopy, X-ray powder diffraction and specific surface area determination.

Depending on the manner of production, we differentiate two basic types of catalysts for the conversion of methane with steam: catalysts obtained by means of impregnation of a preformed support with a solution containing the active component, and catalysts in which the active component and support are produced at the same time.

Although in principle it is believed that there is no reaction between the metal and the support, and that the support is not catalytically active by definition, the manner of putting the metal on the support can essentially influence the properties of the ready catalyst and its changes during application in an industrial reactor [1]. This ex-

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amination involved a commercial catalyst in which the active component was transferred to the α-alumina support by impregnation.

Differential thermal analysis was applied to examine the thermal decompositions of nickel chloride, nitrate, sulphate and hydroxide, used to produce nickel as active component by impregnation [2], the thermal decomposition of nickel nitrate hexahydrate, the process of nickel oxidation [3], and examination of model systems of reforming catalyst and compounds which arise in their preparations [4–8]. X-ray powder diffraction has frequently been used to study the products of the decomposition of these systems. Putanov et al. [4, 5] applied IR spectroscopy to examine model systems, but we have not encountered the application of thermal methods of IR spectroscopy during studies of real systems of reforming catalysts, or of the changes in commercial catalysts in industrial reactors.

Experimental

It is well known that the working conditions are not the same throughout the whole length of the reformer tube, that the working temperature varies from the top to the bottom, and that local overheating is possible. The resulting changes in the catalyst must differ in the various stages of the reformer tube after various times.

The samples for examination were taken after 3, 8, 9 and 20 months of catalyst use, from seven different levels of the reformer tube ranging from the top of the bottom. A total of twenty samples were taken. The scheme of their positions in the reformer tube and the durations of use is shown in Table 1.

In addition to the samples mentioned in Table 1, an unused sample of the same catalyst, denoted "+" was subjected to examinations too.

All samples were studied on a MOM derivatograph, from ambient temperature up to 1000°, at a heating rate of 10 deg/min, in static air atmosphere, with preliminarily heated alumina as reference material.

Table 1 Durations of use, and positions in reformer tube, of tested samples of reforming catalyst

Distance of sample from top of reformer tube, m	Duration of use of catalyst in industrial reactor, months			
	3	8	9	20
	Sample notation			
4.35		10		20
5.80		9		19
7,25	2+	8	11	18+
8.70		7		17
10.15		6		16
11.60		5		15+
bottom	3+	4+	12+	14

A Perkin–Elmer DSC-1B differential scanning calorimeter was used for examinations from ambient temperature up to 500° in a dynamic atmosphere of hydrogen. Determinations of the specific heat capacities of the catalysts were made in the temperature interval 85–125°.

Molecular spectra were studied with a Perkin–Elmer 21 IR spectrophotometer in the wavenumber region 650–5000 cm^{-1}, and on a Perkin–Elmer 377 instrument in the wavenumber region 400–5000 cm^{-1}. The finely powdered sample of catalyst, in a quantity of 0.94–2.0% by mass, was mixed with potassium bromide, and a tablet with a diameter of 7 mm was formed by pressing. The content of catalyst was 0.12–0.26 mg. The samples investigated are indicated by "+" in Table 1.

Samples 1, 2, 4, 7, 8, 9, 10 and 14 were subjected to specific surface area determinations with Perkin–Elmer 212 D sorptionmeter.

Results and discussion

Differential thermal analysis showed that the catalyst support was α-alumina, and that the active component was in the form of γ-nickel oxide, which do not change in the temperature interval of examination. Since the unused catalyst contains 73.52% Al_2O_3, 24.4% NiO, 0.35% Fe_2O_3, 0.08% MgO, 2 ppm CaO and 2 ppm K_2O, the present components could not cause changes which the thermal analysis would register.

The X-ray diffraction structural analysis of this sample confirmed the presence of α-alumina and nickel oxide, but it also pointed to the presence of nickel aluminate [9].

All samples used in the industrial reactor were subjected to thermal analysis. The TG curves of these samples show an insignificant loss of weight (under 1% by mass) up to 300°, due to the removal of free water. Above 400°, all samples reveal the oxydation of metallic nickel, accompanied by a marked exothermic peak in the DTA curve and by an increase of weight according to TG analysis.

Differential thermal analysis of samples used for 8 months (samples 4 to 10) demonstrated oxydation of nickel in the temperature interval 400–800°, with peak temperature at 620–670°. Determination of the surface of the peak of metallic nickel oxydation and its change as a function of the sample position in the catalyst tube did reveal any regularity.

TG analysis showed the increase in sample weight due to nickel oxidation to be 2.37–3.79% (by mass), which corresponds to a metallic nickel content of 8.66–13.82% (by mass). The concentration of metallic nickel tended to increase from the top of the reformer tube to the bottom.

For samples used for 20 months in the reactor (samples 14 to 20), in contrast to the samples used in the reactor for 8 months, the oxidation of metallic nickel begins at higher temperatures, 680–750°, and finishes at 950°. The peak temperature of oxidation ranges from 800° to 850°. The content of metallic nickel, determined by TG analysis is lower than in samples used for 8 months and varies from 0.88 to

7.55% (by mass), again demonstrating a tendency to increase from the top to the bottom of the reformer tube.

The changes in the metallic nickel content as a function of the sample position in the reformer tube during 8 and 20 months of use are shown in Fig. 1. Although the nickel content increases from the top to the bottom of the reformer tube for both groups of samples, the forms of the dependence show a clear difference. While the nickel content of samples from the middle to the bottom of the reformer tube are practically the same after 8 months, after 20 months the samples from the bottom show a rapid jump in nickel content relative to the other tested samples along the tube.

The X-ray diffraction analysis of samples 20 and 14, after 9 months of use in the industrial reactor, shows the presence of metallic nickel (as did the thermal analysis), but it also points to the presence of nickel oxide and nickel aluminate. The phases of metal nickel and nickel oxide are well crystalline in these samples [9].

The temperature changes of the beginning and the maximum of the oxidation peak for the samples after 3, 8, 9 and 20 months of use in the middle (7.25 m) and at the bottom of the reformer tube are illustrated in Fig. 2. The results show a rapid jump of temperatures between 8 and 9 months of use, which is difficult to explain. The temperatures relating to the samples used for 3, 9 and 20 months (not the samples used for 8 months) reveal a weak tendency to a temperature increase for the beginning and the maximum of the oxidation peak with the increase of duration of use, for both the middle and the bottom of the reformer tube, the temperatures at the bottom being a little higher.

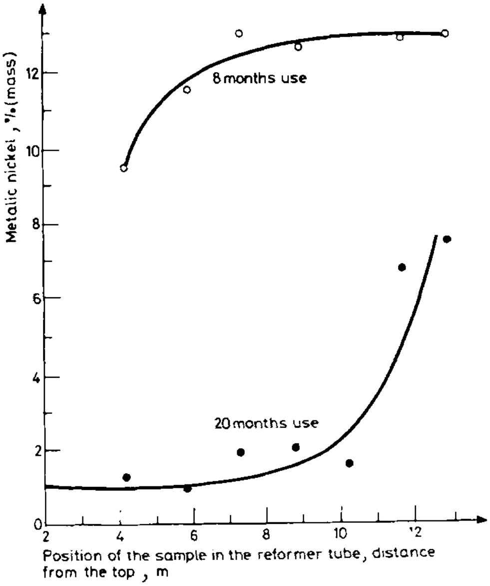

Fig. 1 Changes in metallic nickel contents of catalyst samples as a function of the position in the reformer tube

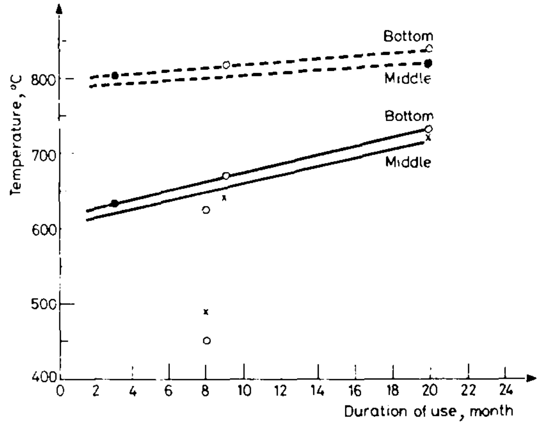

Fig. 2 Changes in temperatures of beginning (———) and maximum (— — —) of oxidation peak as a function of the duration of use of the catalyst in an industrial reactor

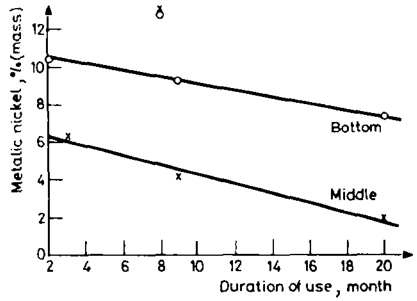

Fig. 3 Changes in metallic nickel content as a function of the duration of use of the catalyst

The increase in temperature of the beginning and the maximum of the oxidation peak for nickel shows the change in the metallic nickel dispersion with increase of the duration of use of the catalyst, the crystals becoming larger. The difference in the temperatures of samples used for 8 months is certainly a consequence of some disturbance in the process, that happened immediately before sampling. This is shown by the temperatures of the beginning and the maximum of the oxidation peak for nickel, which are higher at the top than at the bottom of the reformer tube only in these samples.

The changes in the metallic nickel content as a function of the duration of use for samples from the middle and from the bottom of the reformer tube also show the deviation of samples used for 8 months. Except for these, the content of metallic nickel shows a tendency to decrease with increase of the duration of use for both tested sample positions in the reformer tube, the nickel content being higher at the bottom (Fig. 3). The DTA peaks of nickel oxidation show a clear tendency to decrease with increasing duration of use of the samples (Figs 4–5).

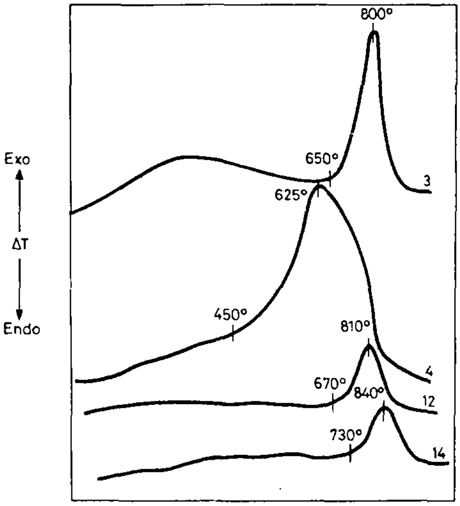

Fig. 4 DTA curves of samples taken from bottom of reformer tube; 3 – 3 months, 4 – 8 months, 12 – 9 months, 14 – 20 months

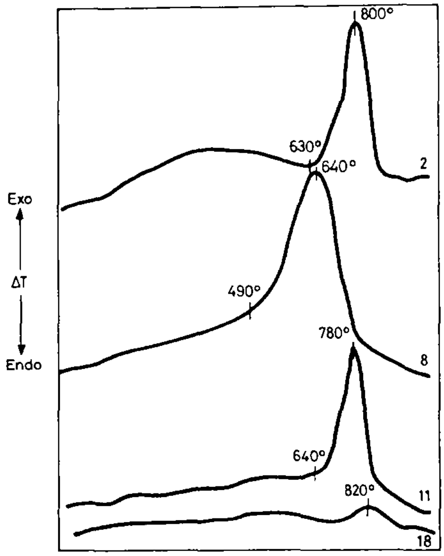

Fig. 5 DTA curves of samples taken 7.25 m from top of reformer tube; 2 – 3 months, 8 – 8 months, 11 – 9 months, 18 – 20 months

Since the nickel in the samples is present as metallic nickel, nickel oxide and nickel aluminate, while DTA and TG analysis permit determination of the quantity of metallic nickel, we set out to determine by DSC the nickel present as nickel oxide in a hydrogen stream. Knowing the contents of metallic nickel, nickel oxide and nickel aluminate, we could follow the changes in the various forms of nickel in the catalyst as a function of the duration of use and of the position in the reformer tube. However, in the temperature interval from ambient temperature up to 500°, we did not succeed in carrying out the reduction of a new sample, for which we expected that a higher temperature of reduction is necessary because of the presence of nickel aluminate. However, we could not register the reduction of nickel oxide for used samples of catalysts either, although according to the literature this starts above 150°, with a peak temperature of reduction of 250° [3]. The energy of nickel oxide reduction is 16.74 J/g, that should be registered under our examination conditions. Because of this, the reduction of nickel oxide in this catalyst will be the subject of further examinations.

With the purpose of explaining the process of reduction, DSC analysis was carried out on the catalysts for preliminary determination of the specific heat at constant pressure. The specific heat at constant pressure for unused catalyst was determined in the temperature interval 102–117° and was 0.8698–0.8706 J/g deg. The same sample was also heated from ambient temperature 500° in a stream of hydrogen, then cooled in a stream of hydrogen to ambient temperature, and the specific heat at constant pressure was determined. The obtained values lay in the range 0.7675–0.7682 J/g deg. This fact shows that nickel oxide present in unused catalyst is practically reduced to the metallic form.

The examinations of samples used in the production process reveal a small difference in specific heat at constant pressure before and after the reduction. This can be explained by the higher temperatures of catalyst reduction in the reformer tube on moving from top to bottom; this is also shown by the increase in the temperature of oxidation, as determined by DTA analysis.

The results of determination of specific surface areas of samples are shown in Table 2. The specific surface area of unused catalyst was 7.77 m^2/g.

Due to the possible deviations of some determinations because of the inhomogenity of the tested grain of catalyst, it is not possible to speak about the regularity of the specific surface area change along the reformer tube for sample used for 8 months.

However, if the change in specific surface area is studied as a function of the duration of use of this catalyst, regardless of the small number of samples, there is a clear tendency of the specific surface area to decrease with increase of the duration of use. The graphical illustration of this dependence shows how the specific surface area of the catalyst decreases rapidly till 8 months of use, and then changes insignificantly up to 20 months. This rapid decrease of the specific surface area with time is believed to be a consequence of the changes noted above for the samples for 8 months (Fig. 6).

The tendency to change of the specific surface area of this catalyst with increasing duration of use is in accordance with the change in the concentration of metallic nickel. The decrease in the active catalyst with the increase of duration of use means that the concentration of metallic nickel and the specific surface area of this catalyst can be used for the rough estimation of its activity.

Table 2 Specific surface areas of samples as a function of the duration of use and their position in the reformer tube

Distance of sample from top of reformer tube, m	Duration of use of catalysts in industrial reactor, months			
	3	8	9	20
	Specific surface area of samples m^2/g			
4.35		1.23		–
5.80		1.04		–
7.25	5.48	0.95	–	–
8.70		1.13		–
10.15		–		–
11.60		–		
bottom	–	1.33	–	0.59

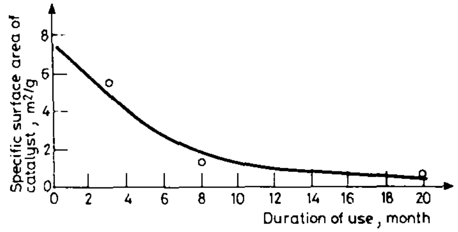

Fig. 6 Changes in specific surface area catalyst as a function of duration of use in an industrial reactor

The IR spectra of the catalyst samples show a series of absorption maxima in the interval 400–900 cm^{-1}, poorly expressed maxima at 1630 and 2850 cm^{-1}, and a marked, prolonged maximum at 340 cm^{-1}.

In contrast to the prolonged absorption maximum found by Putanov [4, 5] for a synthesized spinel of nickel aluminate, our spectra show clear maxima at 450, 660, 640 and 750 cm^{-1}. The spectra do not show any difference between samples, at different heights in the reactor tube.

The samples after 20 months of use show unchanged absorption maxima compared with those of the unused catalyst (Fig. 7).

Conclusions

From these studies on the catalyst for conversion of methane with steam, i.e. nickel oxide on α-alumina as support as a function of the duration of use and its position in the industrial reactor, the following conclusions were drawn:

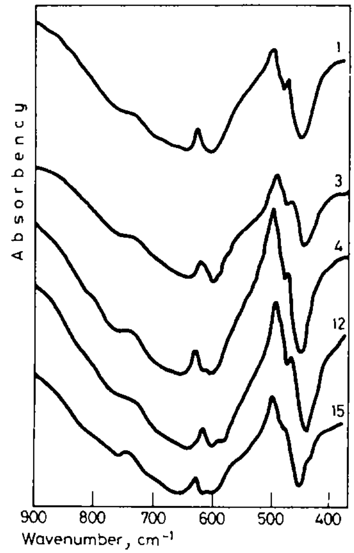

Fig. 7 IR spectra of catalyst samples

1. The content of nickel in the tested samples, determined by means of TG analysis, increases from the top to the bottom of the reformer tube, and decreases with increase of the duration of use.

2. The temperatures of the beginning and the maximum of the oxidation peak of nickel in the tested samples show a tendency to increase with increase of duration of use.

3. The specific surface area does not show a regular change along the reformer tube, but it shows a clear tendency to decrease with increase of duration of use.

4. The concentration of metallic nickel and the specific surface area can be used for the rough estimation of the activity of this catalyst.

5. The changes in nickel aluminate in the samples are registered by means of IR spectroscopy.

6. Differential thermal analysis and thermogravimetric analysis can be used to follow the changes in the active component of this catalyst (nickel) as a function of the duration of use and the position in the industrial reactor.

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Zusammenfassung — Veränderungen der aktiven Komponente eines kommerziellen Katalysators zur Methanreformierung mittels Wasserdampf wurden in Abhängigkeit von der Betriebsdauer und der Lage im industriellen Reaktor untersucht. Proben für die Untersuchung wurden nach 3-, 8-, 9- und 20-monatiger Betriebsdauer aus 7 verschiedenen Höhen vom Boden bis zum Kopf des Reformer-Rohres entnommen. Veränderungen des Katalysators wurden mittels DTA, TG, IR-Spektroskopie, Röntgendiffraktometrie und Oberflächenmessungen verfolgt.

Резюме — Проведено исследование изменений активной компоненты катализатора, используемого в крекинге метана, обработкой его парами в зависимости от продолжительности его использования и расположения его в реакторе. Для исследования были взяты образцы катализатора после 3, 8, 9 и 20 месячного его использования и из различных мест его расположения в крекинг-трубе, начиная с ее верхней части и кончая самой нижней. Для установления процессов изменения катализатора, были использованы методы ДТА, ТГ, ИК спектроскопии, рентгенофазового анализа, а также определения площади поверхности.