

STRUCTURAL STUDIES OF NICKEL-BASED RANEY CATALYSTS

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Electron microscopy and Mössbauer spectroscopy studies of nickel-based Raney catalysts have revealed that the catalysts are formed through the successive aggregation of their structural elements. Catalyst particles are covered by a thin layer of nickel oxide.

Методами электронной микроскопии и ядерной гаммарезонансной спектроскопии исследованы катализаторы Ренея на основе никеля. Установлено, что формирование катализатора осуществляется путём последовательной агрегации его структурных элементов. Частицы катализатора покрыты тонким слоем окиси никеля.

The activity, selectivity, stability and other properties of Raney catalysts are known to be greatly influenced by their chemical and phase composition, type of crystal aggregation and dispersity. We have carried out electron microscopy and Mössbauer spectroscopy studies of the structure and phase composition of these catalysts prepared from nickel- and aluminium-based alloys with Mo, Fe, Cr and Cu additives for the alkylanthraquinone hydrogenation in the production of hydrogen peroxide /1/. Both freshly prepared catalysts and those additionally treated by alkali in an autoclave at 433 K have been studied. This treatment increased the selectivity of the process up to 100%. Iron and nickel contents in the catalysts were 2-15 and 75-90%, respectively. For Mössbauer studies ^{57}Fe isotope instead of usual iron was introduced into the catalysts. Mössbauer spectra were recorded on an electrodynamic-type spectrometer at constant acceleration of the 100 mCi $^{57}\text{Co}(\text{Cr})$ source with an accuracy ranging within 0.02-0.03 mm/s. The maximum rate of pulses was 10^6 pulses/channel. Spectra were recorded at the temperature of liquid nitrogen in a special cryostat. Mössbauer spectra were processed on a BESM-6 computer according to the least-squares method.

Electron microscopy studies were carried out on a UEMV-100 LM microscope. Catalysts were first dispersed in a UZDN-2 ultrasonic apparatus in 100% ethanol and then one drop of the suspension was placed on a grid covered by a collodion film.

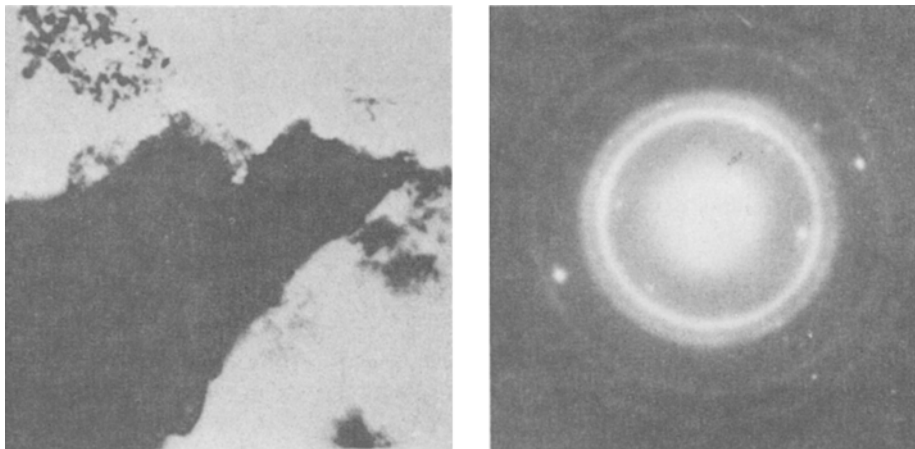


Fig. 1. a, b Electron micrograph and electron diffraction pattern of the freshly prepared catalyst, x 40 000

The micrograph of the freshly prepared catalyst and the respective microdiffraction pattern are illustrated in Fig. 1a, b. The electron diffraction pattern (Fig. 1b) indicates that the catalyst particle is a nickel polycrystal. The spots originate from NiO, and the particle in Fig. 1a can be suggested to be a porous agglomerate of smaller particles with interlayers of NiO and other metal oxides [2]. A micrograph of the passivated catalyst is illustrated in Fig. 2a together with a thin layer with attached particles.

From the electron diffraction pattern (Fig. 2b), it is evident that these are polycrystalline nickel particles on a thin layer of NiO detached from the catalyst particle under ultrasonic treatment. One of the typical objects revealed by the electron microscopy is a needle-shaped structure (Fig. 3). Apparently, it is an oxide with dark spots of a metal phase over it (unfortunately, ring patterns of this structure have not been obtained).

The Mössbauer spectrum of the passivated catalyst is illustrated in Fig. 4. It is a relaxation spectrum of magnetic origin having an effective magnetic field $H_{\text{eff}} = 215$ kOe with a superimposed paramagnetic component whose Mössbauer parameters are $\delta E_1 = 0.65$ and $\Delta E_Q = 0.84$ mm/s. A comparison of the magnetic and the paramagnetic components [3] permits to draw the conclusion that iron is present in the catalyst in the form of two modifications of Fe_2O_3 , i.e. $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{NiO}$ in the ratio of 30 : 70 (according to the calculated ratio of the areas of paramagnetic and magnetic components).

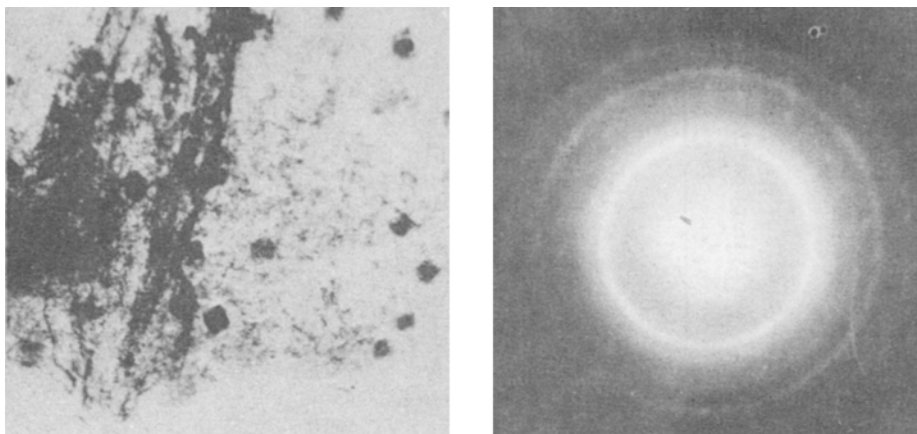


Fig. 2. a, b Electron micrograph and electron diffraction pattern of the passivated catalyst, x 40 000

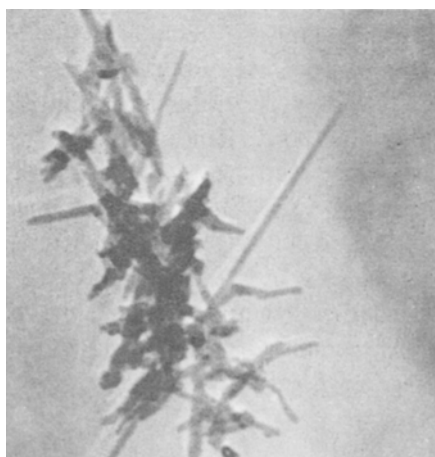


Fig. 3. Micrograph of the passivated catalyst x 50 000

A comparison of Mössbauer spectroscopy and electron microscopy data (Figs 1 and 2) leads to the conclusion that the catalyst particles whose size is greater than 1μ are covered by a thin layer of NiO. According to the Mössbauer studies, this serves as a support for the dispersed Fe_2O_3 and appears to be more extended than the oxide with the metallic nickel particles on it. A part of nickel together with the particles of oxides of the alloying additives is bound with Al_2O_3 (Fig. 3). The

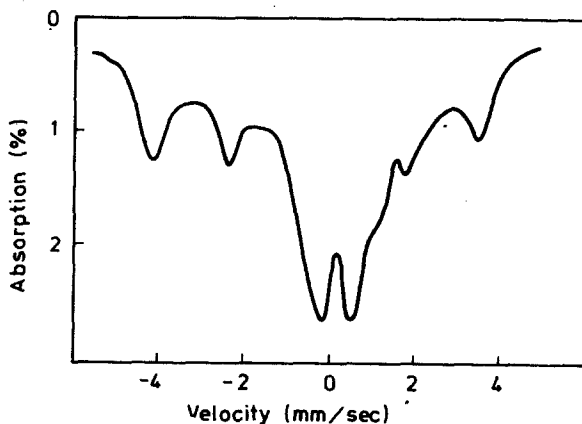


Fig. 4. Mössbauer absorption spectrum of the passivated catalyst

catalyst particle itself is an agglomerate of smaller particles ($\sim 500 \text{ \AA}$) (Fig. 2). These granules are loose particles formed due to the coalescence of nickel crystals and the oxides of the alloying additives. According to the Mössbauer data, the size of iron oxide particles is $\sim 90 \text{ \AA}$ /4/. According to Ref. /5/, the error in the dispersity determination can be $\pm 20 \text{ \AA}$. The sizes of granule-producing nickel crystals (Fig. 2a) are ranging within $40\text{--}100 \text{ \AA}$. Hence, the model of Raney catalyst formation that has been discussed recently /6/ appears to have been proved. According to this model, the successive aggregation of structural elements, i.e. crystals ($10\text{--}100 \text{ \AA}$) to granules ($500\text{--}50\,000 \text{ \AA}$), and granules to agglomerates (1μ) and then to particles of more than 1μ in size takes place. The specific feature of the passivated catalysts is their higher stability. Moreover, the oxide layer on these catalysts is more stable, which permits to observe the NiO layer detached from the catalyst particle, that serves as an extraction replica.

REFERENCES

1. A. B. Fasman, Zh. A. Ikhsanov, N. A. Maksimova, S. D. Mikhailenko, V. Ya. Kitaigorodskaya, L. V. Pavlyukevich: Sov. Pat. 931221, Bull. Izobr., 20, 23 (1982).
2. A. B. Fasman, D. V. Sokolskii, V. F. Timofeeva, D. K. Bazhakov, G. A. Pushkareva: Proc. Intern. Symposium RILEM/UPAC, Final Report, Part 1, p. 1385, Academia, Prague, 1974.
3. A. S. Khlystov, A. V. Kuzminov, L. M. Dautov, G. K. Alekseeva, G. N. Kotova, B. T. Nadykto: Proc. Institute of Organic Catalysis and Electrochemistry, Akad. Nauk Kaz. SSR, 9, 139 (1974).
4. A. M. van der Kraan: Proc. 5th Intern. Conference on Mössbauer Spectroscopy, part 3, p. 723, Bratislava, Czechoslovakia, 1973.
5. W. Kundig, H. Bömmel, G. Constabaris, H. Lindquist: Phys. Rev., 142, 327 (1966).
6. A. B. Fasman: In Catalytic Reactions in Liquid Phase p. 260. Nauka, Alma-Ata, 1980.