

chen Schmelze bei 600—700°C untersucht. Durch Extrapolation ihrer Ergebnisse erhält man bei 570°C den Wert der ersten Assoziationskonstanten $K_1 \cong 30$. Wie hieraus hervorgeht, ist die Assoziation der Chloridionen mit Kupfer(I)-ionen in diesen Schmelzen etwas größer als die Assoziation mit Silberionen.

Untersucht man den Einfluß des Ligandencharakters auf die Ionenassoziation mit Chlorid- und Bromidionen in Alkalichloridschmelzen, dann ist aus den gefundenen Werten die Ähnlichkeit mit den wäßrigen Lösungen offensichtlich, wo gilt, daß die Bromidionen vom thermodynamischen Gesichtspunkt aus stabilere Komplexe bilden als die Chloridionen. Diese Schlußfolgerungen stehen in Übereinstimmung mit der Untersuchung der Assoziation in Alkalinitratschmelzen². Wie aus den angeführten Angaben ersichtlich ist, sind die grundlegenden komplexbildenden Eigenschaften der Ionen in den geschmolzenen Salzen und wäßrigen Lösungen im Prinzip wahrscheinlich nicht verschieden.

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INFLUENCE OF IONIZING RADIATION ON THE CATALYTIC ACTIVITY OF IRON CATALYSTS FOR AMMONIA SYNTHESIS

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Influence of ionizing radiation on synthesis of ammonia was studied by Coekelbergs, Cruceq, and Frennet¹. These authors found a positive influence on the synthesis of the external β -radiation of $^{90}\text{Sr} + ^{90}\text{Y}$ in the presence of microporous alumina.

The aim of this paper was to investigate, from the point of view of practical applications, the effects of the following factors on the catalytic activity: activation in the nuclear reactor, incorporation of the β -nuclide ^{90}Y , and irradiation by the γ -nuclide ^{60}Co . Kinetic data were obtained using a flow, non-pressure arrangement; orientation data were obtained by means of a pressure apparatus at the pressure of 300 atp using a gas mixture of stoichiometric composition.

EXPERIMENTAL

The catalytic activity of catalysts was determined by measuring the extent of the conversion of the stoichiometric mixture nitrogen-hydrogen to ammonia in a flow apparatus (described by Sokol²) at the normal pressure. The temperature of the reactor was kept constant within $\pm 2^\circ\text{C}$. The amount of water in the gaseous mixture (which indicates — besides others — the extent of reduction of the catalyst) was followed by determining the dew point.

The catalysts (granulation 0.25–0.50) were reduced by the nitrogen-hydrogen mixture at a throughput about $100\,000\text{ hour}^{-1}$ and a pressure about 0.10 atp. The temperature was gradually increased from 405°C with one hour stops at the temperatures 405, 430, 455, 480, and 490°C . After the reduction temperature 490°C was reached, the extent of reduction was determined from the dew point. The catalyst was regarded as reduced, if water concentration in the gas beyond the reactor was smaller than 10 p.p.m.

After the catalyst was reduced, the flow of the nitrogen-hydrogen mixture was diminished so that the throughput was about $20\,000\text{ hour}^{-1}$. Concentration of ammonia at the output of the reactor was determined at several temperatures ranging between 350 and 450°C .

The activity of the catalyst was estimated according to the value of the ammonia decomposition constant k determined from the integrated equation as derived by Temkin and Pyžev^{3–8} for the ammonia synthesis. The maximum relative error of the determination was about 15%. The relation derived by Temkin⁹ was used to calculate the constants during the pressure test. Values

TABLE I
Rate Constant k and Activation Energy E_A of the Standard Catalysts
Bulk weight, g ml^{-1} : KM 1 2.02, KM 2 2.08.

Type	$k \cdot 10^{-3}, \text{atm}^{0.5} \text{h}^{-1}$					E_A $\text{kcal} \cdot \text{mol}^{-1}$
	350°C	375°C	400°C	425°C	450°C	
KM 1	0.395	1.246	4.00	9.71	31.6	37.8
KM 2	0.303	0.940	2.63	6.46	23.4	36.0

TABLE II
Laboratory Test of KM 1 Irradiated in the Nuclear Reactor

Integral dose $\cdot 10^{-16}$ n cm^{-2}	$k \cdot 10^{-3}, \text{atm}^{0.5} \text{h}^{-1}$				E_A $\text{kcal} \cdot \text{mol}^{-1}$
	350°C	375°C	400°C	450°C	
7.2	0.078	0.33	1.21	20.8	45.7
21.6	0.18	0.86	3.22	—	47.7
54	0.18	0.70	2.85	—	44.8
108	0.32	1.21	4.21	—	42.7
162	0.18	0.65	2.42	20.1	43.1

of specific radio activity during the activation in the reactor were calculated, as well as the amount of the nuclide ^{90}Zr formed by a radioactive transformation from the nuclide ^{90}Y .

Standard samples of the Swedish catalysts KM 1 and KM 2 were used to check the appropriate arrangement of the experiment (mean values of the rate constant k and of the activation energy E_A are listed in Table I).

Activation of the catalyst KM 1 by thermal neutrons was carried out using the nuclear reactor of the Institute of Nuclear Research, Řež. The time of activation was chosen to be within the range 20–100 hours at the neutron flux $7.5 \cdot 10^{12}$ neutrons $\text{cm}^{-2} \text{s}^{-1}$. The activated samples were tested in the apparatus in the laboratory one week after the irradiation was completed.

Preparation of the sintered catalysts¹⁰ was chosen as a best way of incorporating the nuclide ^{90}Y (as Y_2O_3) — a pure β -emitter.

Pressure tests were used to obtain orientation data on the behaviour of the catalysts (granulation 1.2–1.6 mm) at the pressure 300 atp, and during experiments with syngas used in plant production. Relative error of determinations varied around $\pm 25\%$. Experiments were carried out simultaneously in two reactors heated to the same temperature and filled with the tested sample and the standard sample, respectively. Throughputs varied between $6 \cdot 10^4$ – 10^5 h^{-1} , both during the reduction and the experiment.

TABLE III

Laboratory Test of Sintered KM 1 + 5% Y_2O_3

Bulk weight, g ml^{-1} : samples 1–4 1.80, samples 5 and 6 1.75.

Sample	$k \cdot 10^{-3}, \text{atm}^{0.5} \text{h}^{-1}$					E_A kcal . mol ⁻¹	A_{spec} mCi . g ⁻¹	Zr content . 10^3 $\mu\text{g}(\text{Zr}) \cdot \text{g}^{-1}$
	375°C	385°C	400°C	410°C	425°C			
S 1	1.84	4.14	6.31	10.9	23.1	44.5	6.4	3.5
S 2	1.49	2.48	5.04	8.2	16.6	43.5	4.7	6.7
S 3	1.49	2.49	5.27	8.55	18.4	43.6	2.9	10
S 4	1.34	2.25	4.61	7.32	17.8	42.8	1.4	13
S 5	0.79	1.61	3.62	6.60	14.5	51.0	—	—
S 6	0.68	1.17	2.72	5.34	11.8	52.0	—	—

TABLE IV

Influence of γ -radiation on KM 1

Bulk weight 2.12 g ml^{-1} did not change after irradiation; weight 10.0 g; throughput $65\,000 \text{ h}^{-1}$
Activation energies, kcal . mol⁻¹: 38.0; after irradiation 38.1.

Temperature, °C	40	425	450	475	487	500
$k \cdot 10^{-3}, \text{atm}^{0.5} \text{h}^{-1}$	2.4	8.5	23	51	81	100
$k_{\text{irr}} \cdot 10^{-3}, \text{atm}^{0.5} \text{h}^{-1}$	2.6	8.8	25	56	69	95

In order to determine the influence of the earlier irradiation of the catalyst KM 1 by the γ -nuclide ^{60}Co , the sample of the KM1 catalyst was irradiated prior to the experiment in the Gamma-cell (Institute for Research, Production, and Use of Radioisotopes) by a γ -radiation dose comparable in absorbed intensity to that of the β -radiation of ^{90}Y .

RESULTS AND DISCUSSION

It follows from the values of the rate constant (Table II) that in practically all cases and at all temperatures studied the activation in the reactor resulted in a decrease of the values of the rate constants, and in an increase of the corresponding activation energies as compared to the non-irradiated catalyst. However, factors effecting the system of the iron catalyst in the nuclear reactor are complex, and the experimental data obtained do not allow for specifying reasons of the observed decrease. Spectrometric analysis showed that the activated catalyst contained the following nuclides: ^{24}Na , ^{26}Al , ^{28}Al , ^{42}K , ^{45}Ca , ^{47}Ca , ^{56}Mn , ^{55}Fe , ^{59}Fe , ^{64}Cu .

By incorporating ^{90}Y , a pure β -emitter with a relatively high energy of β -radiation ($E_{\beta} = 2.26$ MeV) was introduced into the KM 1 catalyst. Yttrium oxide acts as a slightly positive promotor.

In all cases (Table III) a higher catalytic activity was obtained for radioactive catalysts than for both nonradioactive sintered catalysts and the standards KM 1 and KM 2. The catalytic activity of the sintered catalysts decreased with the decreasing radioactivity. This decrease was not caused by a gradual passivation when storing the samples, as the values of the activation energy did not change.

Traces of interstitial ^{90}Zr formed in a nuclear reaction play practically no role: this is evidently because of small amounts of this substance.

Irradiation by γ -radiation prior to the experiment was used to specify the influence of the pure γ -nuclide ^{60}Co on the iron catalyst (Table IV). Doses of absorbed γ -radiation varied between 20–50 Mr. It can be said that no effect was observed, within the experimental error of the pressure test, even with fairly high doses of γ -radiation. Evidently, no healing (permanent as far as the temperature stability is concerned) of the surface active centers occurs in the iron catalyst for ammonia synthesis over the region of doses studied.

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