EFFECT OF THE IONIZING RADIATION ON THE CATALYTIC ACTIVITY OF THE BASF K-3-10 CATALYST IN THE LOW-TEMPERATURE CONVERSION OF CARBON MONOXIDE BY WATER VAPOUR. CATALYTIC ACTIVITY OF THE PRE-IRRADIATED CATALYST

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The catalytic activity of the BASF K-3-10 catalyst with regard to the low-temperature conversion of carbon monoxide by water vapour and its changes after irradiation of the contact area by gamma or beta radiation or by fast neutrons has been investigated. The irradiated samples exhibit a moderately or even substantially higher catalytic activity in comparison with the non-irradiated catalyst, the change being dependent on the absorbed dose; moreover, the effective activation energy of the reaction increases, too. Important differences in the action of different types of the ionizing radiation used have been observed and their probable explanation is offered. In course of these experiments the catalysts were analyzed and the specific surface of the catalyst was measured at various stages of their history. It has been found that at all stages the specific surfaces of the irradiated catalyst are equal to the respective specific surfaces of the non-irradiated contacts.

The catalytic conversion of carbon monoxide by water vapour,

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$
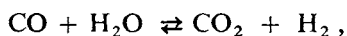
is one of the most common industrial catalytic processes and at the present time it represents the cheapest industrial source of hydrogen. With regard to the present problems with power resources and also due to the ecological problems the importance of this reaction can be expected to increase. It seemed therefore interesting to investigate the possibility of any positive effects of the ionizing radiation on the course of this reaction because only very few papers were so far published dealing with the radiation modification of the catalytic activity of the solid phase with regard to this conversion reaction[1,2]. Schroeder and Zabrzeski[1] studied this reaction using Fe_2O_3–Cr_2O_3 and CuO–CoO catalysts with the radionuclide ^{32}P incorporated into the catalytically inactive component of the catalyst bed and they observed an increase of the catalytic activity with the increasing radioactivity of the bed. An increase of the catalytic activity of the Czechoslovak industrial Fe_2O_3–Cr_2O_3 catalyst

after an introduction of a radioactive component into the catalyst bed was also reported by the workers of this Laboratory[2]. The same catalyst pre-irradiated by gamma or beta radiation, or eventually by fast neutrons, exhibits a non-monotonous dependence of the catalytic activity on the absorbed dose of various types of radiations. At the same time a low stability of the radiation-induced catalytic effects was observed[2]. Because the decrease of the reaction temperature usually increases the stability of the radiation catalytic effects, it seemed worthwhile to study the effects of pre-irradiation on the catalytic activity of the BASF K-3-10 contact catalyst that is sufficiently active already at about 450 K, while the working temperature of other iron- and chromium oxide catalysts lies by about 200—400 K higher, depending on their type.

EXPERIMENTAL

The reaction of carbon monoxide with water vapour was followed using the flow tubular reactor working in the integral regime. Catalyst of the grain size of 0·8—1 mm was used; the standard procedure of the catalyst preparation was as follows: 2 g of the catalyst were mixed with 4 g of silica glass of the same grain size. Before the measurements the catalyst was reduced for 140 min by the nitrogen–hydrogen mixture; the hydrogen content gradually increased with the simultaneous increase of the temperature from 493·2 K to 533 K. The flow rate of the reducing mixture was 2·2 mol/h. After complete reduction, the following reaction conditions were adjusted: the reaction temperature $T_R = 493·2$ K, the saturation temperature of the initial gas mixture by water vapour $T_S = 348·4$ K (the partial water vapour pressure $p_{H_2O}^0 = 33·6$ kPa), the reactor pressure $p = 0·103$ MPa, the input of the carbon monoxide and nitrogen mixture $Q = 3·15$ mol/h, the molar ratio of carbon monoxide x_{CO}^0 in this mixture 0·2. Under these conditions the catalyst was treated for 120 min in order to achieve its full reduction by carbon monoxide and to reach the catalytic activity that would be stable during the test. Only after this treatment started the test of the catalytic activity that consisted of the measurement of the dependence of the carbon monoxide conversion degree α_{CO} on the input of the initial mixture. All other conditions remained the same as during the stabilization (conditioning) period. The conversion degree was determined for five different values of the initial mixture input ranging from 3·15 mol/h to 10·75 mol/h.

Finally, the first value was determined again so that the stability of the catalytic activity could be verified. Samples of the dry initial mixture and of the converted one were taken in given time intervals. The content of oxides was determined using the Orsat apparatus; carbon dioxide was absorbed in the potassium hydroxide solution and carbon monoxide was absorbed in the solution of cuprous and ammonium chlorides.

The catalyst was analyzed semiquantitatively using the emission spectroscopy, the main components (Cu, Zn, Cr) were then analyzed quantitatively using complexometry. The catalyst was transferred into the solution using the decomposition by acid vapours in an autoclave at elevated temperature and pressure. The specific surface was determined by the method of nitrogen desorption at the room temperature; liquid nitrogen was used as the adsorption bath. The specific surfaces were measured for the catalysts in the initial (original) state, after reduction, after the stabilization of the catalytic activity and after the test itself, both for the non-irradiated contact catalyst and several chosen irradiated samples.

⠆ The catalysts were irradiated by ^{60}Co gamma rays, by beta radiation from the [90]Sr-^{90}Y source and by fast neutrons from the [252]Cf source. The dose rate of the ^{60}Co source was deter-

mined using the Fricke dose meter, the dose rate of the beta particle source was calculated and the doses in the ^{252}Cf source were calculated from the data given by the producer. The irradiation was carried out in the presence of air and at the room temperature, under the same conditions also the irradiated samples were kept before testing that began 24—36 hours after irradiation.

The experimental data were treated in the following way: the values of the carbon monoxide conversion degree α_{CO} for various flow rates of the reaction mixture were plotted against the respective contact times (i.e., the mean values of the reactant retention in the catalyst bed). The contact time τ is defined by the equation

$$\tau = V_{free}/\dot{V}_{CO} , \qquad (1)$$

where $\dot{V}_{CO}$ is the volume flow rate of carbon monoxide (m^3/h) and V_{free} is the free volume of the catalyst (m^3). The value of the catalyst free volume was not measured but it can be assumed that it is the same for all samples under study (the same type of the contact catalyst, the same treatment) so that the contact times can be expressed by a conventional time unit ξ defined as follows: if the reaction in the system proceeds at the temperature of 473·15 K, at the pressure of 0·103 MPa and at the catalyst loading of 1 mol of CO/h.g, the contact time is equal exactly 1ξ. Because all experiments were carried out at the pressure of 0·103 MPa, the contact times τ can be expressed in ξ units using Eq. (2), where m is the weight of the catalyst in g, the meaning of all other symbols was already explained:

$$\tau(\xi) = m . 473·15/Q . x_{CO}^0 . T_R . \qquad (2)$$

It was found that the experimental dependence $\alpha_{CO} = f(\tau)$, (Fig. 1) can be very well fitted by the kinetic equation for the reversible reaction of the first order,

$$\alpha_{CO} = \alpha_r(1 - \exp(-k\tau/\alpha_r)) , \qquad (3)$$

where $k(\xi^{-1})$ is the rate constant of the reaction in the forward direction and α_r is the equilibrium conversion degree. Under the conditions of the catalyst testing ($T_R = 493·2$ K, the molar ratios of the reaction components entering the reaction $x_{H_2O}^0 : x_{CO}^0 : x_{N_2}^0 = 3 : 1 : 4$) the equilibrium
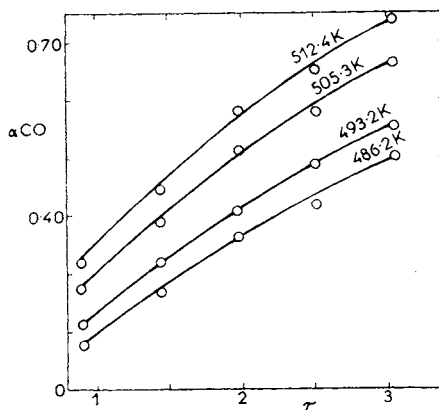

FIG. 1

The transformation degree α_{CO} as a function of the contact time $\tau(\xi)$ for the non-irradiated catalyst at different temperatures

conversion degree α_r is close to unity, the reaction can be assumed to be practically irreversible and Eq. (3) is simplified to

$$\alpha_{CO} = 1 - \exp(-k\tau). \tag{4}$$

Analysis of the measurement errors revealed that the standard deviation of the rate constant determination as obtained from the experimental values of α_{CO} and τ by the linear regression of $\ln(1 - \alpha_{CO}) = f(\tau)$ correspond to the possibilities of the adopted method up to about 4%. Because this deviation did not exceed substantially this limit for both the non-irradiated and ir-radiated samples, their catalytic activities were compared on the basis of the relative catalytic activity C_{rel}, defined by

$$C_{rel} = k/k_{st}, \tag{5}$$

where k and k_{st} are the rate constants for the irradiated and non-irradiated catalysts, respectively, calculated from the experimental dependences $\alpha_{CO} = f(\tau)$ by the procedure described above. For all catalysts, non-irradiated as well as irradiated, it can be stated that during the standard catalytic test their activities do not decrease under the limit given by experimental errors.

RESULTS AND DISCUSSION

Based on the results of analysis the most probable composition of the catalyst calcinated at 773·2 K in the presence of air to the constant weight is given in Table I. The remainder, insoluble in acids (most probably graphite), amounts to about 2 wt.%. From other elements aluminium and magnesium were determined by the semi-quantitative spectral analysis. Their content was roughly estimated to be from 0·5 to 1·5 wt. % for each element; with regard to their low abundance other methods than the complexometric titrations should be used for their more precise determination. Spectroscopy revealed the presence of many other elements the contents of which lie within 10^{-1} to 10^{-3} wt. % and these elements are evidently not intentionally introduced components. Spinel $ZnO . Cr_2O_3$ was found in the sample calcinated at 773·2 K by X-ray diffraction; however, it was found neither in the

TABLE I

The most probable composition of the catalyst calcinated in the presence of air at 773·2 K

Element	Abundance (wt. %)	Compound	Abundance (wt. %)
Cu	47·2	CuO	59·1
Zn	19·4	ZnO	24·1 — 0·35x
Cr	7·8	Cr_2O_3	11·3 — 0·65x
		$ZnO . Cr_2O_3$	x
Sum	74·4		94·5

sample calcinated at 573·2 K nor in the treated catalyst, nor in the catalyst after the standard test. Chromium sesquioxide (Cr_2O_3) was not detected by X-ray diffraction in any of the samples under study, which indicates its high dispersion in the system; the non-calcinated non-reduced catalyst gave several other weak diffuse reflections that can be ascribed to the not fully calcinated intermediates from the preparation of the contact catalyst because they disappeared during the following treatment. Thermogravimetry of the catalyst reduction by hydrogen at 533·2 K showed that under these conditions 30·2% of CuO is reduced to copper; more extensive reduction by carbon monoxide is probable, but it can be expected that due to the presence of chromium sesquioxide it is not completely reduced to copper[3]. The reduction of zinc oxide under the conditions of the catalyst introduction into the reaction and in the presence of chromium sesquioxide can be neglected[4,5].

The specific surface measurements showed that the pre-irradiation of the non-reduced catalyst by gamma radiation with doses up to 1·5 MGy, by beta radiation up to 3·5 MGy, and by fast neutrons up to 2 kGy does not change the value of the specific surface. Also after the standard reduction, after the conditioning and testing of the catalytic activity of irradiated samples the specific surfaces have the same value as in the non-irradiated catalyst. This result is in agreement with the present state of our knowledge, because — according to Coekelbergs[6] — effects of this type are improbable even after irradiation in the nuclear reactor up to the doses of 10^7 Gy. The commercial type of the catalyst has the specific surface of 74·0 m^2/g while the catalyst after the standard testing of the catalytic activity had only 50·3 m^2/g. It was found that the specific surface decreases during both the catalyst reduction and the conditioning period; during the standard catalytic test the specific surface remains unchanged within the experimental errors. It is therefore probable that even the working surface area of the contact catalyst does not change during the catalytic activity test. The specific surface decrease in course of the catalyst conditioning by the reaction mixture can be evidently ascribed to the proceeding reduction by carbon monoxide. The specific surface decrease of the samples under study during their reduction and conditioning indicates unequivocally also the decrease of the absolute area of their surfaces because no increase of the contact catalyst weight can be expected during these processes. This conclusion is in agreement with the results of other studies obtained for similar catalysts with relatively high content of copper[7]; on the other hand, in catalysts with a low copper content an increase of their surfaces was observed[8,9]. This can be probably explained by a closer contact between the Cu(CuO) crystallites on the surface as well as between the grains of zinc oxide in the catalysts with a high content of copper, by their aggregation and easier sintering[10].

The catalytic activity measurements of the pre-irradiated samples showed that the irradiation of non-reduced catalysts by all types of radiation used either does not change or slightly increases their catalytic activity, depending, however, on the absorbed dose.

The relative catalytic activity, C_{rel}, as a function of the absorbed dose of beta radiation (Fig. 2) and neutron radiation (Fig. 3) at the reaction temperature $T = = 493.2$ K has distinct maxima at the absorbed doses of 63 kGy to 126 kGy (beta radiation) and 1.1 kGy (fast neutrons). The maximum values of C_{rel} are in both cases comparable and they lie in the range from 1.7 to 1.8. The catalytic activity of gamma irradiated samples (Fig. 2) increased at first with the absorbed dose and at $D \doteq 35$ kGy the maximum value of $C_{rel} \doteq 1.5$ was reached which did not change towards higher doses. The catalytic activities C_{rel} of samples irradiated by the doses of 5.4 kGy of gamma radiation, 1.7 kGy of beta radiation or 0.37 kGy of fast neutrons are very similar and they lie in the interval from 1.3 to 1.4. It can be concluded that for the same radiation catalytic effect about 14 times higher doses of gamma radiation and 5 times higher doses of beta radiation are required in comparison with fast neutron irradiations. The fact that the primary radiation defects are reflected in the final properties of the catalyst, in spite of reduction and conditioning processes, indicates undoubtedly that the catalytic activity dependence on the absorbed dose is given by the charge state of the initial non-reduced system. This follows from the remarkable radiation-catalytic effects induced by gamma and beta radiations when the formation of charge defects during the irradiation predominates. Changes of the catalytic activity due to the fast neutron irradiation could be expected because
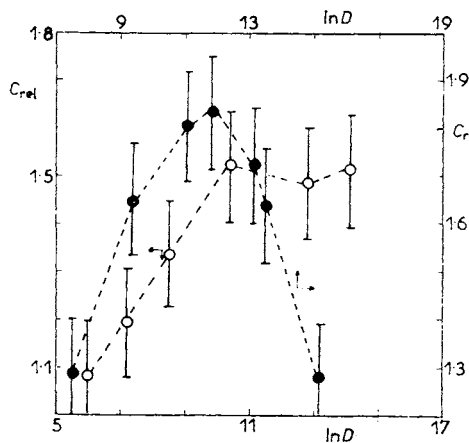

FIG. 2

The relative catalytic activity C_{rel} at $T = = 493.2$ K as a function of the absorbed dose D of the beta (●) and gamma (○) radiations
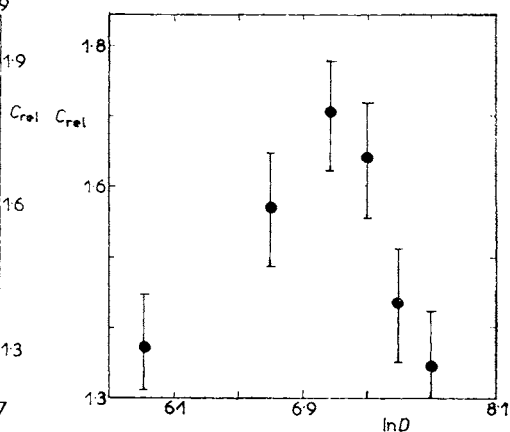
FIG. 3

The relative catalytic activity C_{rel} at $T = = 493.2$ K as a function of the absorbed dose D of fast neutrons

the defect formation probability on the crystalline lattice level is by 2—7 orders of magnitude higher (depending on the atomic number of the target) than for the beta and gamma radiations and, moreover, these defects are substantially more stable than the charge defects. At the same time increases also the probability of the charge defect stabilization on point defects. Together with the induced radio-activity observed in samples irradiated by neutrons, all these factors can play an important role in the catalytic activity changes[6]. The existence of maxima (Figs 2 and 3) is evidently connected with the fact that within certain limits of absorbed doses an optimum charge state of the irradiated substance is achieved with regard to the formation (or radiation modification) of the precursors of catalytically active centers[11]. In course of further irradiation this state is disturbed which results in the decrease of the catalytic activity.

In the case that the processes of the formation and disappearance (positive and negative modifications) of the catalytic centers precursors are in equilibrium in suf-ficiently wide dose limits, the "saturation" of the radiation-catalytic effect can be established (Fig. 2, C_{rel} as a function of the gamma radiation dose). Different shapes of the dependences in Fig. 2 evidently indicate differences in processes by which the primary effects induced by gamma and beta radiations are transformed into the changes of the catalytic properties. One possible reason for the observed differences could be connected with different distributions of charged defects, produced by the two types of radiation, between the surface and bulk of the irradiated substance; in the case of gamma radiation this distribution is much more homogeneous whereas beta radiation has a more pronounced effect on the charge state of the crystalline surfaces of the catalyst components. The formation rate of the catalytic centers precursors on the surface will be higher in the latter case and it is probable that the equilibrium between the formation and disappearance of precursors will be achieved at their higher surface concentrations, to which corresponds also the higher maximum value of the radiation-catalytic effect induced by beta radiation. If the active center precursor is represented, *e.g.*, by an electron stabilized on a point defect, this electron can be "knocked out" from the potential well by another electron or photon. If this electron does not recombine again with the point defect, the precursor disappears. Assuming the formation of a higher charge non-equilibrium between the surface and the bulk of the solid in the case of beta irradiation than in the case of gamma irradiation, it can be expected that — after the maximum surface concentration of precursors is achieved — the processes of their disappearance will predominate earlier (at lower absorbed doses) than in the other case; the probability of the pre-cursor decomposition on the catalyst surface will be greater due to their higher surface concentration and, moreover, the probability of their reconstitution will decrease because the released electron will migrate into the bulk of the solid and contribute to the charge equilibrium reestablishment. In this way it is possible to interprete qualitatively the narrower region of the radiation stability and the higher

value of the radiation-catalytic effect induced by beta radiation. The remarkable effect of fast neutrons on the catalytic activity already at rather low values of the absorbed doses can be ascribed to the specific effects of neutron radiation mentioned above; the fact that the maximum on the dose dependence (Fig. 3) is very narrow in comparison with the dependences obtained for the other types of radiation can be caused — along with the processes discussed above — by the so called "polishing effect" that is characteristic for neutrons[6,11].

The comparison of the values of absorbed doses for individual types of ionizing radiation used and of the respective radiation-catalytic effects observed could indicate that the catalyst sensitivity towards radiation increases in the sequence: gamma, beta, fast neutrons. However, it cannot be excluded that the resulting radiation-catalytic effect depends not only on the properties of the radiation used but also on the dose rate that was very different for the sources used; it amounted to 3 098 Gy/h for gamma radiation, to 20 973 Gy/h for beta radiation and to 0·26 Gy/h for fast neutrons. Because the construction of the ^{90}Sr-^{90}Y source allows to irradiate also at the half dose rate, one sample was irradiated by the maximum rate and another one with the half dose rate. The total absorbed dose was in both cases 125·9 kGy. The standard test of the catalytic activity yielded the following values of the relative catalytic activities at 493·2 K: 1·83 ± 0·10 for the first sample and 1·74 ± 0·08 for the second one. It can be therefore concluded that the decrease of the beta radiation dose rate by 50% has no effect on the resulting radiation-catalytic effect and that only the total absorbed dose is relevant, which is in agreement also with other studies[11]. The general validity of this statement should be, however, verified in a much wider range of dose rates.

With several samples the dependence of the transformation degree of carbon monoxide on the temperature was measured at a constant reaction mixture input. Using the equations (4) and (2) the reaction rate constants were calculated and the effective activation energies E_A of the reaction were estimated. In spite of considerable errors of the E_A determinations by this fast method — the standard deviations amounted up to about 7% — it was possible to conclude that the pre-irradiation of the catalyst does not change (or increase) the effective activation energy of the reaction; the values of E_A obtained ranged from 55 kJ/mol to 100 kJ/mol, while for the non-irradiated catalyst the analysis of the dependence $\alpha_{CO} = f(\tau)$ (Fig. 1) yielded the value of $E_A = 52·8 ± 2·2$ kJ/mol. Moreover, it has been found that the samples with higher E_A value exhibit — almost without exception — a higher catalytic activity at 493·2 K than the samples with lower values of E_A. From these facts it can be concluded that: a) the character of the catalytically active reaction centers is changed due to the catalyst irradiation, and b) after irradiation a compensation effect can be observed in the system.

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