

# 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. STABILITY OF THE RADIATION CATALYTIC EFFECTS

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The radiation catalytic properties of the BASF K-3-10 catalyst were studied, namely the dependence of these effects on the time interval between the catalyst irradiation and the reaction itself and also on the length of the catalyst use. The catalytic effects decrease exponentially with the interval between the irradiation and the reaction if the catalyst is kept in the presence of air. The stability of effects induced by various types of radiations increases in the sequence beta radiation — gamma radiation — fast neutrons. The radiation catalytic effect stability in the reaction increases in the same sequence.

One of the factors limiting the exploitation of positive radiation catalytic effects is their time stability. This is given by the recovering processes proceeding in the irradiated catalyst during the period prior to the reaction and during the reaction itself. Moreover, the dependence of the radiation catalytic effect on the time of the catalyst use can be even more complicated; the radiation modified catalytic activity need not be either constant or decrease monotonously with the time of use but it can exhibit substantial changes even after a rather long induction period (after tens of hours) as it was observed by Clarke<sup>1</sup> in the case of the Fischer-Tropsch synthesis over an irradiated catalyst. Also in this Laboratory we have found differences in the behaviour of the irradiated sample of the Czechoslovak conversion catalyst on the basis of ferric oxide-chromic sesquioxide only after about 30 working hours<sup>2</sup>. The rate of recovering processes proceeding in the irradiated catalyst preceding its use in the reaction and therefore also the resulting radiation catalytic effect can depend very strongly on the atmosphere under which the catalyst is kept before its use; this effect was observed, *e.g.*, in the hydrogenation of nitrobenzene over the irradiated cuprous catalysts<sup>3</sup>.

It seemed therefore worthwhile to study in detail the radiation catalytic effects induced by pre-irradiation of the BASF K-3-10 catalyst, by various types of ionizing radiations, as they were described in our previous paper<sup>4</sup>, also from this point of view.

## EXPERIMENTAL

The catalytic activity of samples was tested using a flow integral reactor and the dependence of the conversion degree  $\alpha_{\text{CO}}$  of carbon monoxide on the contact time was measured. The contact

time  $\tau$  was expressed by Eq. (1) using the time units  $\xi$  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 to 1  $\xi$ ,

$$\tau(\xi) = m \cdot 473.15 / Q x_{\text{CO}}^0 T_{\text{R}}, \quad (1)$$

where  $m$  is the catalyst weight in g,  $Q$  is the input of the nitrogen and carbon monoxide mixture (mol/h),  $x_{\text{CO}}^0$  is the molar ratio of carbon monoxide in the  $\text{N}_2 + \text{CO}$  mixture, and  $T_{\text{R}}$  is the reaction temperature (K). The rate constants  $k(\xi^{-1})$  of the reaction were then calculated from the experimental dependence  $\alpha_{\text{CO}} = f(\tau)$  and from the kinetic equation

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

The catalytic activity of individual samples was compared using the relative catalytic activities,  $C_{\text{rel}} = k/k_{\text{st}}$ , where  $k_{\text{st}}$  is the rate constant of the reaction proceeding over a standard unirradiated catalyst. The standard testing of the catalytic activity proceeded under the following conditions: the reaction temperature  $T_{\text{R}} = 493.2$  K, the molar ratio of the components in the initial reaction mixture  $X_{\text{H}_2\text{O}}^0 : X_{\text{CO}}^0 : X_{\text{N}_2}^0 = 3 : 1 : 4$ . The contact time  $\tau$  varied within 0.9 and 3  $\xi$ . The catalyst reduction, stabilization of its catalytic activity, and the standard testing procedure were described in detail in the paper<sup>4</sup>. The dependence of the radiation catalytic effect on the time interval between irradiation and the catalytic reaction was studied using the irradiated samples that were kept in the irradiation vessels in air and at the room temperature. After the given time interval elapsed, the standard test<sup>4</sup> was made.

The long-term studies of the catalytic activity proceeded as follows: after the standard reduction and the catalyst pre-treatment the dependence of  $\alpha_{\text{CO}} = f(\tau)$  was measured in the following time intervals after the reduction: 2 h—4 h 40 min, 26 h—28 h 40 min, and 50 h—52 h 40 min. Between the measurements of this dependence the conversion degree of carbon monoxide at the contact time of 3.05  $\xi$  was repeatedly determined in two-hour intervals. The reaction temperature was 493.2 K during the whole experiment. The specific surface area of the catalysts was measured by the low-temperature adsorption of nitrogen.

## RESULTS AND DISCUSSION

Three samples were used for the study of the effect of the time interval between the irradiation and the reaction on the radiation catalytic activity: the catalyst irradiated by the  $^{60}\text{Co}$  gamma radiation by a dose of 35.6 kGy (Sample No 1), by the  $^{90}\text{Sr}$ — $^{90}\text{Y}$  beta radiation by a dose of 62.9 kGy (Sample No 2), and by the fast neutrons from the  $^{252}\text{Cf}$  source, with a total dose of 0.77 kGy (Sample No 3). Due to the limited irradiation capacity of the  $^{252}\text{Cf}$  source only one repeated determination of the catalytic activity could be made with the Sample No 3; altogether five measurements were made with the Samples No 1 and 2 in various time intervals. The results of the catalytic activity measurements are summarized in Table I. The first column gives the time elapsed between the irradiation and the beginning of the measurement. Fig. 1 presents the values of  $\ln(C_{\text{rel}} - 1)$  for the Samples No 1 and 2 as a function of this time interval.

From these results it follows that the relative catalytic activities of all samples decrease with the time interval after irradiation. The linear character of the de-

pendences presented in Fig. 1 for the Samples No 1 and 2 is very good and their regression yields the following values for the half-lives of the disappearance of the radiation catalytic effects:  $26.4 \pm 0.7$  days for the Sample No 1 and  $13.7 \pm 0.5$  days for the Sample No 2. Assuming the same time dependence of  $\ln(C_{rel} - 1)$ , the half-life of the disappearance of the effect in the sample irradiated by fast neutrons can be estimated to about 38 days.

TABLE I

Dependence of the catalytic activity on the time interval between irradiation and the catalytic reaction

Days	$C_{rel}$		
	Sample 1	Sample 2	Sample 3
1	$1.52 \pm 0.06$	$1.80 \pm 0.11$	$1.58 \pm 0.11$
5	$1.45 \pm 0.09$	$1.68 \pm 0.10$	
11	$1.34 \pm 0.08$		
12		$1.42 \pm 0.08$	
15			$1.44 \pm 0.08$
30		$1.20 \pm 0.07$	
47	$1.15 \pm 0.07$		
51		$1.06 \pm 0.07$	
86	$1.05 \pm 0.06$		

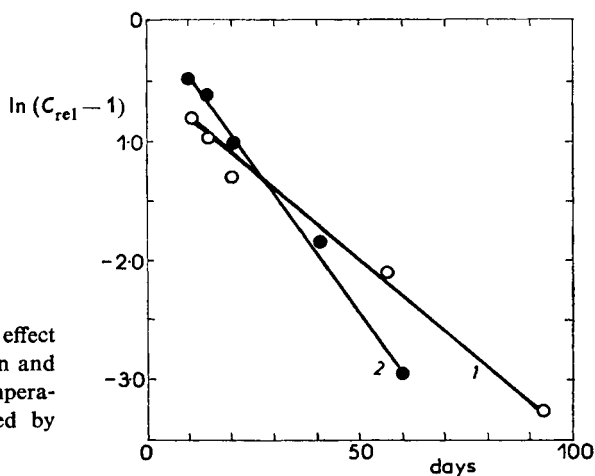


FIG. 1

Dependence of the radiation catalytic effect on the time interval between irradiation and the catalytic reaction at the reaction temperature of 493.2 K for samples irradiated by gamma (1) and beta (2) radiations

The effect of the environment on the recovery of the irradiated catalyst was studied using the following experiment: the catalyst was irradiated by the same dose of beta radiation as the Sample No 2 (62.9 kGy) and immediately after the irradiation it was transferred into a glass tube, the tube was evacuated several times, filled with pure nitrogen, and then sealed off. This sample was kept at the room temperature for 30 days and then it was tested for its catalytic activity and the experiment gave the value of  $C_{rel} = 1.51 \pm 0.08$ . This value is substantially higher than the analogous value for the Sample No 2 and the time interval  $t = 30$  days in Table I ( $C_{rel} = 1.2$ ) and the half-life of the effect disappearance can be estimated to about 46 days. It is therefore evident that the change of atmosphere increases significantly the stability of the primary radiation changes responsible for the final radiation catalytic effects.

The stability of the radiation-modified catalytic activity on the pre-treated (activated) catalyst was studied using an analogous procedure. The sample irradiated similarly as the Sample No 2 was reduced, its catalytic activity was stabilized and the catalytic bed was cooled down to the room temperature in the flow of nitrogen. The reactor was then dismantled from the apparatus, thoroughly washed with pure nitrogen and then hermetically sealed. The catalytic bed was kept at the room temperature for 30 days, with occasional washing with nitrogen. 30 days after irradiation the reactor was inserted (under the flow of the mixture of nitrogen with carbon monoxide) into the preheated jacket, the saturation with water vapour started and – when the standard test conditions were established – the catalytic activity was measured. This experiment yielded the value of  $C_{rel} = 1.71 \pm 0.09$ . The specific surface area of the catalyst after the experiment was  $52.0 \text{ m}^2/\text{g}$ . The comparison with the results of the previous experiment shows that the catalytic activity of this sample is by about 13% higher and only insignificantly lower than the activity of the similarly irradiated sample, tested by the standard procedure one day after irradiation (Table I, Sample No 2). It can be concluded that in contrast to the catalysts kept in air or in nitrogen in the non-reduced form, the time interval between the irradiation and the catalytic reaction has no effect on the final radiation catalytic effect if the catalytic activity is stabilized immediately after irradiation and the catalyst is kept in the absence of air. The obtained value of the specific surface area ( $52 \text{ m}^2/\text{g}$ ) is in agreement – within the measurement error – with the mean value of the specific surface area after the standard test ( $50.3 \text{ m}^2/\text{g}$ ) and it indicates that no significant changes of the physico-chemical properties of the catalyst can be ascribed to the modified experimental procedure.

Decrease of the final radiation catalytic effect is evidently connected with the recovering processes that consist of the recombination of charge defects in course of which the thermodynamically equilibrium charge state of the irradiated substance is re-established. In the given case these processes are probably connected with the decrease of the number of the radiation modified (“produced” by the radiation) precursors of the catalytically active centers. The acceleration of recovering processes

in the presence of air can be probably ascribed to the effects of oxygen; oxygen molecules, the ground state of which is a triplet state so that they can act as biradicals, have a well-known high affinity towards electrons (and radicals) and very easily enter into the radiation-induced processes (also during the post-irradiation period). Therefore even very small amounts of oxygen can have a significant effect on the kinetics of annealing processes and subsequently also on the kinetics of the disappearance of the radiation catalytic effects. Moreover, it is well known that the irradiation of oxides results in a substantial change of the content of the non-stoichiometrically bound oxygen, the amount of which depends — in the post-irradiation period — on the degree of the primary radiation defects annealing<sup>5,6</sup>. The course of the subsequent reduction and therefore also the catalytic properties of the product can be influenced by the different content of the non-stoichiometric oxygen (there is an experimental evidence in this respect<sup>7</sup>). *E.g.*, if the content of non-stoichiometric oxygen is increased (decreased) by irradiation, it is evident that in the course of post-irradiation effects its content will decrease more slowly (increase more rapidly) in the medium with a higher partial pressure of oxygen. Hence, if the radiation catalytic effect is governed — at least partially — by the changes of the non-stoichiometric oxygen content, the changes of the atmosphere are reflected also in the rate of its disappearance. Although this behaviour was observed only in the case of a sample irradiated by beta radiation, the same effect can be probably expected even after gamma irradiation because the primary radiation changes have the same nature in both cases. The more remarkable is the difference in the half-lives of the disappearance of the effects induced by the two types of radiations. There is no other possibility but to look for the reasons of this effect in the different primary radiation defect distribution between the surface and bulk of the irradiated material and in the consequent differences of the volume–surface interactions<sup>4</sup>.

The stability of the radiation catalytic properties of the reduced and already used catalyst kept in the nitrogen atmosphere is not surprising. It can be expected that the irradiated catalyst that must be considered as a highly non-equilibrium system (in which spontaneous annealing takes place) will be in a particularly stable state after reduction during which the primary charge defects are undoubtedly thermally annealed. On the other hand, the more remarkable is the fact that the primary radiation defects are reflected in the resulting catalytic activity in spite of the reduction process.

The long-term catalytic activity (Fig. 2) was measured both for the unirradiated catalyst (Sample 0) and for the samples irradiated with a gamma dose of 50.3 kGy (Sample 1), beta dose of 65.5 kGy (Sample 2), and with the fast neutron dose of 1.93 kGy (Sample 3). Table II presents the relative catalytic activities of the irradiated samples that were determined according to the scheme of long-term experiments mentioned above. In the computations the value of  $k_{st}$  in Eq. (3) was replaced by the value of the rate constant corresponding to the reaction in the presence of non-

-irradiated catalyst used after the same time interval as the tested sample. Finally, the specific surface areas of all samples under study were determined and the following results were obtained:  $46.2 \text{ m}^2/\text{g}$  for the Sample 0,  $43.9 \text{ m}^2/\text{g}$  for the Sample 1,  $46.8 \text{ m}^2/\text{g}$  for the Sample 2, and  $45.5 \text{ m}^2/\text{g}$  for the Sample 3. Fig. 2 shows that the conversion degree decreases in all cases monotonously with the working time of the catalyst. This decrease is evidently the fastest in the experiment No 2 (beta radiation); for the Samples No 1 and 3, that are characterized by the practically identical initial catalytic activities, the rates of the decrease are comparable; however, for Sample 3 (fast neutrons) the conversion degree at the end of the test is significantly higher than for the Sample No 1 (gamma radiation). The values of  $C_{rel}$  given in Table II mean that at the end of the experiments the radiation catalytic effect of Samples 1 and 2 undoubtedly vanished while the Sample 3 (fast neutrons) has a higher value of  $C_{rel}$  and a higher catalytic activity is also probable. At the end of the

TABLE II  
Dependence of the catalytic activity of irradiated catalysts on the length of their use

Hours	$C_{rel}$		
	Sample 1	Sample 2	Sample 3
3.33	$1.47 \pm 0.08$	$1.79 \pm 0.10$	$1.58 \pm 0.09$
27.33	$1.23 \pm 0.08$	$1.20 \pm 0.08$	$1.28 \pm 0.08$
51.33	$1.05 \pm 0.07$	$1.01 \pm 0.06$	$1.13 \pm 0.07$

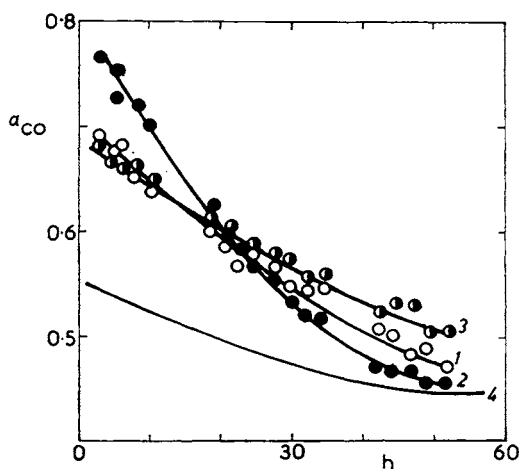


FIG. 2

Dependence of the conversion degree  $\alpha_{CO}$  on the reaction time (in hours) for the unirradiated catalyst (4), gamma irradiated sample (1), beta irradiated sample (2), and sample irradiated by fast neutrons (3) at the reaction temperature  $T = 493.2 \text{ K}$  and at the contact time  $\tau = 3.05\xi$

test the specific surface areas of all samples have the same value (within the error limits) and it can be concluded that the pre-irradiation has no effect on the surface area, even after long working period.

In neither sample the decrease of the catalytic activity in course of the experiments can be fully ascribed to the diminished surface of the catalyst. The specific surface areas of the samples after the test indicate the surface decrease by about 8–9% between the first determination of  $C_{rel}$  and the end of the test (the specific surface areas after the standard test were about  $50 \text{ m}^2/\text{g}$ ), while in the course of the long-term tests the respective catalytic activities decreased by 24, 46, 57, and 40%, respectively (in the given sequence of samples). Whatever the real reasons of the decrease of the non-irradiated catalyst activity may be (there could be other slow changes of the catalyst structure, the conditioning need not be complete in the moment of the measurement), the reasons for the significantly faster decrease of the irradiated catalyst activity could be the following: *a*) the catalytically active centers (modified by radiation or formed during the pre-irradiation) are in course of the reaction more labile than the original centers. The idea of a different nature of the original and radiation-modified centers is partially corroborated by the observed increase of the effective activation energy of the reaction due to the pre-irradiation of the catalyst<sup>4</sup>; however, this criterion cannot be considered as unambiguous; *b*) due to the high catalytic activity of the samples their working surface is thermally more stressed (it is locally overheated) so that the catalytic centers are more rapidly thermally destroyed and the activity of these contact catalysts decreases also more rapidly.

However, the more detailed explanation of the cause of the radiation catalytic disappearance (it may be caused even by a combination of the processes mentioned above) would require other experiments. The enhanced value of  $C_{rel}$  at the end of the experiment with Sample 3 (Table II) means rather unambiguously that the radiation catalytic effect induced by fast neutrons is relatively more stable. The explanation of this fact should be sought in the specific effects of the neutron radiation discussed above. The dependence illustrated in Fig. 2 indicates the lowest stability of the radiation catalytic effect induced by beta radiation; however, if the processes mentioned under *b*) predominate in the catalyst deactivation, the conclusion on the lower stability of modified centers need not be correct. The highest decrease of the catalytic activity would be subject to the condition that the radiation catalytic effect in the sample under study is the highest, *i.e.*, that this catalyst has the highest surface concentration of the catalytically active centers (from the results of the paper<sup>4</sup> it follows that the effective activation energy of the reaction over the Sample 3 will be either equal or higher than that over other samples and in any case higher than over the unirradiated catalyst). However, from Fig. 2 it can be seen that after about 25 hours of the reaction, when the conversion degree of carbon monoxide is practically the same for all irradiated samples, the dependence for the Sample 2 (beta radiation) decreases more rapidly; the lower stability of centers modified by

beta radiation is probable so that the stability increases in the sequence: beta radiation – gamma radiation – fast neutrons.

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