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## EFFECT OF THE RADIONUCLIDE $^{32}\text{P}$ INCORPORATION ON THE CATALYTICAL ACTIVITY OF THE BASF K-3-10 CATALYST FOR THE LOW-TEMPERATURE CONVERSION OF CARBON MONOXIDE BY WATER VAPOUR

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The catalytical activity of the BASF K-3-10 catalyst for the low-temperature conversion of carbon monoxide by water vapour has been studied in dependence on the activity of incorporated radionuclide  $^{32}\text{P}$ . Radioactivity of the catalytical bed ranged from 0 to 630 MBq of incorporated  $^{32}\text{P}$ . It has been observed that at first the catalytical activity increases with the increasing activity of  $^{32}\text{P}$  and finally it reaches a limit value that is by about 50 per cent higher than that of the same non-radioactive catalyst. The comparison of these results with those obtained in the studies of the catalytical activity of the same catalyst pre-irradiated by  $\beta$  radiation of the  $^{90}\text{Sr}$ - $^{90}\text{Y}$  source revealed that in the case of radioactive beds the observed positive radiation-catalytical effect can be ascribed to the pre-irradiation of the catalyst (during the period between the preparation of the radioactive catalytical bed and the catalytical reduction itself) and to the interactions of the ionizing radiation with the catalyst during the subsequent operations. The radiation-catalytical effects induced by the two processes mentioned above differ substantially by their time stability. The probable explanation of the nature of these two effects is proposed using the published mechanism of this reaction.

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In our previous studies<sup>1-3</sup> it has been found that the pre-irradiation of the non-reduced BASF K-3-10 catalyst with various types of ionizing radiation leads to a substantial increase of its catalytical activity. However, the catalytical activity of the radiation modified catalyst decreased rather rapidly during the reaction and gradually reached the activity of the unirradiated catalyst<sup>2</sup>. Calcination of the irradiated non-reduced catalyst, and in a lesser degree also the calcination of irradiated reduced catalysts resulted in a decrease of the final radiation-catalytical effect<sup>3</sup>. This behaviour is one of the main obstacles for the practical use of the observed effects. However, a continuous irradiation of the catalyst in situ, i.e., during the reaction, is an obvious modification of the radiation-catalytical reaction. This can be achieved by the following three processes: a) by external irradiation of the catalytical bed, when the bed and the radiation source are separated; b) by internal irradiation, i.e., by using a radioactive catalyst; and c) by incorporation of the radioactive source

into the catalytically inactive component of the bed that is then mixed with the catalyst itself.

If the catalytical activity is changed by the irradiation during the reaction, it can be expected that the resulting radiation-catalytical effect could be of a higher duration in comparison with pre-irradiated catalysts. An increase of the catalytical activity for the conversion of carbon monoxide on a radioactive catalytical bed with the radionuclide  $^{32}\text{P}$ , i.e., in the variant *c*), was already observed in both the low-temperature catalyst of the  $\text{CuO-CoO}$  type (cf. ref.<sup>4</sup>), and in the high-temperature contact catalyst on the basis of  $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$  (cf. refs.<sup>4,5</sup>). It seemed therefore interesting to extend the previous studies<sup>1-3</sup> of the radiation-catalytical effects on the low-temperature conversion catalyst BASF K-3-10 by investigations of the modification mentioned above.

## EXPERIMENTAL

The catalytical activity of samples under study was measured in an integral flow reactor at the temperature  $T_R = 493.2\text{ K}$ , at the pressure  $p = 0.103\text{ MPa}$ , and at the molar ratios of the initial reaction mixture components  $x_{\text{H}_2\text{O}}^0 : x_{\text{CO}}^0 : x_{\text{N}_2}^0 = 3 : 1 : 4$ . The mixture input ranged from 3.15 to 10.75 mol/h. The catalytical bed consisted of 2 g of the catalyst, of the grain size of 0.8–1.0 mm, and of 4 g of fused silica of the same grain size (the standard bed); in the radioactive beds 4 g of the phosphate glass with various activities of  $^{32}\text{P}$  was added to the catalyst instead of silica. Prior to the experiments it was verified that the radioactive component as well as fused silica have no catalytical activity with respect to the reaction under study. The values of rate constants on individual beds were obtained by the analysis of the experimental dependence of the carbon monoxide conversion degree on the reaction mixture input (i.e., on the contact time). The relative catalytical activity  $C_{\text{rel}}$ , defined as  $C_{\text{rel}} = k/k_{\text{st}}$ , where  $k_{\text{st}}$  is the rate constant of the reaction proceeding on the standard bed (zero radioactivity, unirradiated catalyst), and  $k$  is the rate constant on the radioactive bed, was used as the measure of the radiation-catalytical effect. The standard test procedure, the following of the catalytical activity for a long period of time, and the treatment of the experimental results were described in our previous studies<sup>1,2</sup>. The catalytically inactive material forming the radioactive component of the beds under study was prepared by the following procedure: chips of an aluminium foil (99.99 per cent of Al) were dissolved in an excess of  $\text{H}_3\text{PO}_4$  and this solution was heated to a honey-like consistence. The substance formed, solid at the room temperature, was further heated and calcinated at the temperature of about 1170 K until a white porous material with traces of local melting was formed. This product was melted in an electrical oven at 1800 K and a transparent glass was obtained with a high content of phosphorus, 27.3 wt. per cent, which approximately corresponds to the stoichiometry of  $\text{AlPO}_4$  (25.4 wt. per cent). Phosphorus was determined gravimetrically as phosphomolybdate; however, the titration determination after alkaline melting of the phosphate glass and after the dissolution of the melt in the hydrochloric acid was made as a control test. Glass prepared by this procedure was crushed, the fraction of the required grain size was separated and irradiated in a nuclear reactor by thermal neutrons for 3.5 h at the neutron flux of  $3 \cdot 10^{12}\text{ m}^2\text{ s}^{-1}$ . The specific activity of the irradiated material at the moment of irradiation termination was 213 MBq/g (the activity was calculated using the cross section  $\sigma = 1.9 \cdot 10^{-29}\text{ m}^2$  for the  $(n, \gamma)$  reaction on the  $^{31}\text{P}$  nucleus). This radioactive material was treated further after a time delay of 150 h (i.e., after the total decay of the radionuclide  $^{24}\text{Na}$ ). The radioactive catalytical

bed was prepared by adding 4 g of the radioactive glass (as measured volumetrically in a calibrated probe) to 2 g of the catalyst in a polyethylene bottle, the bottle was closed, the content thoroughly mixed and transferred into the reactor on a support layer of crushed fused silica. All these operations were made in a modified dust-proof box. With respect to the  $^{32}\text{P}$  nuclide half-life (14.3 day) several beds with gradually decreasing radioactivity were prepared in respective time intervals. Approximate doses absorbed by the catalyst during the period between its contact with the radioactive component and the beginning of the experiment and during the standard test were also obtained by calculation.

## RESULTS AND DISCUSSION

Results obtained for the dependence of the catalytical activity on the radioactivity of the catalytical bed are summarized in Table I. Reduction of beds denoted 1R to 5R began always 30 min after their preparation; in these cases the experiments extended over about 9 h, including also the time required for the adjustment of experimental conditions. The dependence of the carbon monoxide conversion on the mixture input was measured during 160 min after the two-hour period of stabilization of the catalytical activity. Only in the case of the bed 6R the radioactivity of which in the moment of its preparation was equal to that of the bed 5R, the reduction was made 74 days after its preparation so that its radioactivity  $A_1$  in the moment of reduction was lower than the radioactivity of the bed 1R. So in this case the total experiment extended over 1 785 h (measured from the moment of the bed preparation). It was verified that under the conditions of the catalytical activity testing no changes detectable by the analytical method used (the Orsat apparatus) occur in the reaction mixture after passing through the reactor containing only the radioactive component

TABLE I

Dependence of the relative catalytical activity on the catalytical bed radioactivity

| Bed | Catalyst radioactivity, MBq |         | Dose absorbed by the catalyst, Gy |         | Relative catalytical activity $C_{\text{rel}}$ |
|-----|-----------------------------|---------|-----------------------------------|---------|--|
|     | $A_0^a$                     | $A_1^b$ | $D_0^c$                           | $D_1^d$ |  |
| 1R  | 21.1                        | 21.1    | 1.3                               | 23.1    | $1.13 \pm 0.07$                                |
| 2R  | 115.4                       | 115.3   | 7.1                               | 126.1   | $1.33 \pm 0.08$                                |
| 3R  | 319.2                       | 318.9   | 19.6                              | 348.9   | $1.47 \pm 0.09$                                |
| 4R  | 448.2                       | 447.7   | 27.5                              | 489.9   | $1.49 \pm 0.09$                                |
| 5R  | 629.2                       | 628.6   | 38.6                              | 687.8   | $1.54 \pm 0.09$                                |
| 6R  | 629.2                       | 17.4    | 37 163                            | 37 182  | $1.72 \pm 0.10$                                |

<sup>a</sup> In the moment of bed preparation; <sup>b</sup> in the beginning of reduction; <sup>c</sup> prior to reduction; <sup>d</sup> until the test completion.

of the bed. This fact means that the results are affected neither by the catalytical effects of the radioactive component nor by the eventual radiolysis of the reaction mixture. From the data given in Table I it can be seen that the relative catalytical activities  $C_{rel}$  for the beds 1R to 5R increase with the radioactivity of the bed. The steepest increase of  $C_{rel}$  values was observed in the beds 1R to 3R, for which the activity of  $^{32}\text{P}$ , taken relatively to the weight of the catalyst in the non-reduced state, is about  $160 \text{ MBq g}^{-1}$ . With further increase of the activity (beds 3R to 5R) the increase of  $C_{rel}$  is negligible so that with respect to the experimental errors the  $C_{rel}$  values can be considered to be nearly constant and the radiation-catalytical effect reaches its "saturation". Qualitatively the same dependence was observed for the same reaction on the high-temperature  $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$  catalyst<sup>5</sup> and the same behaviour was also described by a group of Polish authors<sup>4</sup> on the  $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$  and  $\text{CuO-CoO}$  catalysts. The bed 6R, the activity  $A_1$  of which was lower than that of the bed 1R but that was significantly irradiated prior to the reduction exhibits the unambiguously highest catalytical activity.

After the first measurement of the catalytical activities the radioactive beds 4R and 6R were kept in contact with the reaction mixture under the conditions described for the long-term experiments<sup>2</sup> and after 24 h another measurement of  $C_{rel} = k/k_{st}$  was made. In this case the value of  $k_{st}$  used for the evaluation of  $C_{rel}$  means the rate constant of the reaction proceeding on the non-radioactive bed containing the catalyst not modified by radiation that was treated for the same period of time under the same conditions as the sample under study. These experiments had to determine the time stability of the radiation-catalytical effects and they are summarized in Table II.

TABLE II

Comparison of the time stability of the catalytical activities of the samples 0 and 1 and of the radioactive beds 4R and 6R

| Time, h | Sample                                      |                 |                 |                 |
|---------|---|-----------------|-----------------|-----------------|
|         | 0   | 1               | 4R              | 6R              |
|         | Relative catalytical activity, $C_{rel}$    |                 |                 |                 |
| 3-33    | 1   | $1.79 \pm 0.10$ | $1.49 \pm 0.09$ | $1.72 \pm 0.10$ |
| 27-33   | 1   | $1.20 \pm 0.08$ | $1.44 \pm 0.08$ | $1.29 \pm 0.08$ |
|         | Relative decrease of the rate constant in % |                 |                 |                 |
| 3-33    | 0   | 0               | 0               | 0               |
| 27-33   | -15.9                                       | -43.6           | -18.8           | -37.8           |

The values of  $\Delta k$  need not correspond to the relative decrease of  $C_{rel}$  as the values of  $k_{st}$  on the standard bed, not modified by radiation, used for the evaluation of  $C_{rel}$  also decrease with the reaction time<sup>2</sup>. The values of  $\Delta k$  and  $C_{rel}$  correspond to the middle of the time interval during which the catalytical activity was tested. The zero of the time scale was set to the beginning of the two-hour stabilization of the catalyst. The relative catalytical activities  $C_{rel}$  for the beds 4R and 6R and for  $t = 3.33$  h are equal to the values of  $C_{rel}$  for these beds in Table I. The standard unirradiated catalyst is denoted by zero and the catalyst pre-irradiated by  $\beta$  radiation of the  $^{90}\text{Sr}$ - $^{90}\text{Y}$  source with the dose 65.5 kGy is denoted by 1. Both these samples were studied for a long period of time in our previous study<sup>2</sup>. From Table II it follows that after 27 h of reaction the catalytical activity of the beds 4R and 6R is still substantially increased. Comparing the values of  $C_{rel}$  it can be seen that the increase of the catalytical activity induced by the introduction of the radioactive component into the bed 4R is relatively nearly the same as that obtained at the beginning of the reaction. On the other hand, the radiation-increased catalytical activity of the bed 6R decreases during the same period of time by about 60 per cent and the value of  $C_{rel}$  drops under the value of  $C_{rel}$  for the bed 4R. The total change of the reaction rate constant  $\Delta k$  on the bed 4R is comparable with the respective value for the unirradiated sample 0 (Table II); for the bed 6R the magnitude of this change is comparable with the value of  $\Delta k$  for the sample No. 1 that was pre-irradiated with a dose of 65.5 kGy of  $\beta$  radiation.

In our previous study<sup>1</sup> it was found that the first significant changes of the catalytical activity caused by pre-irradiation of the catalyst with  $\beta$  radiation can be observed at the dose of about 1.7 kGy (with  $C_{rel} = 1.29 \pm 0.08$ ). Comparing the doses  $D_0$  estimated for the beds 1R to 5R (Table I) with this value it can be concluded that the radiation-catalytical effects observed in the radioactive beds can in no case be ascribed to the irradiation during the period between their preparation and the beginning of the reduction. This statement cannot be affected by the uncertainty of the estimation of the doses  $D_0$  because — assuming the extreme case when all the energy of radiation emitted by  $^{32}\text{P}$  is absorbed by the catalyst — the values of  $D_0$  would rise by about 40 per cent so that  $D_0$  for the bed 5R would be 54 Gy which is a value about 30 times lower than the lower dose limit mentioned above (1.7 kGy). On the other hand, the bed 6R, for which the estimated value of  $D_0 = 37.1$  kGy so that it falls into the region in which rather substantial changes of the catalytical activity have been observed for the pre-irradiated catalysts<sup>1</sup> but the radioactivity of which at the beginning of the reduction is the lowest (cf. Table I), had the highest initial catalytical activity of all the radioactive beds under study and its value of  $C_{rel}$  is practically the same as that of the sample No. 1 (Table II). It is necessary to keep in mind that the values of  $C_{rel}$  of catalysts irradiated with doses from 60 to 600 kGy by the  $^{90}\text{Sr}$ - $^{90}\text{Y}$  source fall into the interval from 1.6 to 1.8. It is therefore very probable that in the case of the bed 6R the radiation-induced increase of the

catalytical activity can be ascribed predominantly to the pre-irradiation of the catalyst. The assumption of the similar genesis of the radiation-catalytical effects both in the  $\beta$  pre-irradiated samples and in the radioactive bed 6R is also corroborated by the results of its stability in time (Table II) as it is evident that the rate of the radiation-modified catalytical activity decrease of the samples 1 and 6R during the reaction is of the same magnitude. The plausible explanation of the effect of the catalyst pre-irradiation on its catalytical activity is presented in the discussion to our previous paper<sup>1</sup>, in the other paper<sup>2</sup> the time instability of the catalytical activity changes induced by this process is also discussed.

The radiation-catalytical effects observed on the beds 1R to 5R can be explained as follows:

- a) by the formation of a surface catalytically more active due to a different mechanism of the catalyst reduction in the field of the ionizing radiation;
- b) by the direct interaction of radiation with the catalyst surface in the course of the reaction itself;
- c) by a combination of the preceding two mechanisms.

In order to be able to correlate, at least qualitatively, the experimental results with the variants mentioned above, certain assumptions with regard to the nature of the catalytically active centers and to the reaction mechanisms have to be adopted. In spite of a number of uncertainties in this respect the reaction mechanism proposed by Boreskov et al.<sup>6-8</sup> seems to be the most probable and experimentally most sustained. According to it the carbon monoxide conversion on the copper-containing catalysts proceeds either via the formation of transient complexes of the carbonate type (the catalytically active centre is in this case formed by the ion-atom pair  $\text{Cu}^+ - \text{Cu}^0$  on the surface of the catalyst) or via the formation of the formate complexes (the active centre is formed by a pair of  $\text{Cu}^+$  ions that must comply with certain steric requirements). Hence, in both cases the catalytical activity will depend first of all on the amount and distribution of  $\text{Cu}^+$  ions on the catalyst surface and both these factors could be affected by the different course of reduction in the field of the ionizing radiation (processes *a*). A large number of experimental data has been accumulated on the effects of the ionizing radiation on the mechanism of reduction of various substances and on the catalytical properties of the resulting product<sup>9</sup>. If only the processes of the type *a*) participate on the reduction, it can be expected that after completing the reduction and after conditioning of the catalyst during which the catalytically more active surface is formed, the irradiation would no more change the catalyst activity. In the light of the adopted reaction mechanism the type *b*) processes can be ascribed to the change of the  $\text{Cu}^+$  ions population that is formed on the surface of the catalyst by the interactions of radiation with reduced copper. The abundance of  $\text{Cu}^+ - \text{Cu}^+$  or  $\text{Cu}^0 - \text{Cu}^+$  pairs increases with the increase of the bed radioactivity (i.e., with the  $\beta$  particle flux) and therefore the catalytical activity

increases, too. In the moment when the maximum possible surface concentration of  $\text{Cu}^+ - \text{Cu}^+$  pairs, complying with the required steric conditions, is achieved, any further increase of the amount of cuprous ions has no effect on the catalytical activity and the radiation-catalytical effect becomes "saturated" (Table II). If the catalytical centre is formed by the  $\text{Cu}^0 - \text{Cu}^+$  pair, any continued formation of cuprous ions could lead to a perturbation of the optimum ratio  $\text{Cu}^0/\text{Cu}^+$  and therefore to a decrease of the catalytical activity. A direct correlation between the catalytical activity of the copper-containing conversion catalysts and the concentration of  $\text{Cu}^+$  ions on their surfaces was in this respect experimentally proved in the already quoted study of Boreskov and coworkers<sup>8</sup>. The radiation catalytical effects induced by the type *a*) processes are given only by the changes of the selective surface area of the catalytically active component (i.e., of copper) that are induced by the effect of radiation on the catalyst during the reduction; the extent of the type *b*) processes is given partly by the surface area of the active component and partly by the  $\beta$  particle flux (i.e., by the radioactivity of the bed) with which it interacts. This approach allows to explain the results of the repeated determination of the bed 4R catalytical activity in the time 27.3 h (Table II). The bed radioactivity decreased by about 5 per cent between the two measurements and this decrease evidently cannot decrease the radiation-catalytical effect. This is also corroborated by the character of the dependence of  $C_{\text{rel}}$  on  $A_1$  in Table II for the beds 1R to 5R. The magnitude of the radiation-catalytical effects, regardless whether it is caused by the processes of the types *a*), *b*) or *c*), will be given by the selective surface area of the catalytically active copper. Because the catalytical activity is directly proportional to the selective surface area of copper, the activity decrease of the standard unirradiated catalyst in the course of the reaction (sample 0, Table II) can be understood as a decrease of the selective surface area of copper resulting from various effects (slow changes of the catalyst structure, blocking of its surface by deposits, etc.). From this approach it follows for the radioactive bed 4R that its catalytical activity will decrease with the catalytical activity of the unirradiated catalyst (cf. values of  $\Delta k$  for samples 0 and 4R, Table II), while the relative value of the radiation catalytical effect will remain unchanged (cf. the values of  $C_{\text{rel}}$  for the samples 0 and 4R, Table II).

## REFERENCES

1. Motl A.: Collect. Czech. Chem. Commun. 51, 279 (1986).
2. Motl A.: Collect. Czech. Chem. Commun. 51, 1571 (1986).
3. Motl A.: Collect. Czech. Chem. Commun. 52, 2383 (1987).
4. Schroeder J., Zabrzski J.: Chem. Stosow. XI, 3A, 253 (1967).
5. Můčka V., Cabicar J., Pospíšil M., Kudláček R., Motl A.: Report on the Project P-09-159-209-03. Faculty of Nuclear and Physical Engineering, Czech Technical University, Prague 1980.
6. Yuryeva T. M., Boreskov G. K., Gruvar V. Sh.: Kinet. Katal. 10, 862 (1969).

7. Davydov A. K., Borekov G. K.: Dokl. Akad. Nauk SSSR 236, 1402 (1977).
8. Borekov G. K., Yuryeva T. M. in: *Teoreticheskie problemy kataliza (Theoretical Problems of Catalysis)*, p. 106. SO AN SSSR, Inst. katal., Novosibirsk 1977.
9. Pospíšil M.: *Thesis*. Czech Technical University, Prague 1975.

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