RADIATION CATALYTICAL EFFECTS IN THE PRE-IRRADIATED AND THERMALLY TREATED CATALYST BASF K-3-10

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The effects of various thermal treatment methods on the radiation catalytical effects, induced by the pre-irradiation of the BASF K-3-10 catalyst by the γ- or β-radiation or by fast neutrons, were investigated. It has been found that the calcination of the irradiated non-reduced catalyst results in a strong decrease or even in total disappearance of the final radiation catalytical effects; however, at the same time the catalytical activity of the unirradiated catalyst was found to increase. The calcination of the catalysts in nitrogen atmosphere after reduction led also to a substantial decrease of the resulting positive radiation catalytical effects and exceeding a certain calcination temperature resulted in the decrease even of the unirradiated catalyst activity. It could be concluded that the calcination in nitrogen of the reduced irradiated samples decreases the radiation catalytical effects less than the calcination on air of the non-reduced irradiated samples. In both cases a different thermal stability of effects induced by different types of the ionizing radiation has been observed and it has been found that it increases in the sequence beta radiation — gamma radiation — fast neutrons. The investigation of the γ radiation dose dependence of the radiation catalytical effect on the catalyst calcinated before irradiation under the access of air showed that the final radiation catalytical effects are lower than those observed in the case of similarly irradiated but non-calcinated samples. At the same time the dose dependence of the effect has the same character in both cases.

In our previous study[1] it has been shown that the catalytical activity of the BASF K-3-10 catalyst in the low-temperature conversion of carbon monoxide by water vapour can be increased by pre-irradiation of the catalyst by different types of the ionizing radiation. The relative increase of the catalytical activity amounted up to about 70% at the reaction temperature of 493·2 K, depending on the absorbed dose and the type of radiation used. In the following study[2] the time stability of the observed radiation catalytical effects was investigated and it was found that *a)* the radiation-induced increase of the catalytical activity falls with the time elapsed between the irradiation and the catalytical reaction; *b)* the radiation catalytical effects fade out even during the catalytical reaction itself; *c)* in both preceding cases the time stability of these effects depends on the type of the radiation applied and increases in the sequence β-radiation — γ-radiation — fast neutrons.

One of the most commonly used methods for detail investigation of the character of radiation catalytical effects is the thermal treatment of the catalyst under study

in different stages of its history. Because the reduced form of the catalyst is catalytically active in the carbon monoxide conversion, it is possible to obtain information on the thermal stability of the radiation modified or radiation produced precursors of the catalytically active centers from the studies of the catalytical activity of samples calcinated between irradiation and reduction. The measurement of the catalytical activity of irradiated samples calcinated after reduction (when the radiation modified catalytically active centers are already formed) gives an information on the thermal stability of these centers as such. The X-ray diffraction studies of the catalyst under study in its commercial form revealed[1] that it contains — along with the main components (CuO, ZnO) — a series of not-fully-calcinated products that disappear after calcination. The effect of the ionizing radiation on the catalytical activity of previously calcinated samples was therefore investigated with the aim to find out in what degree the presence of these compounds affects the radiation catalytical effects described above.

EXPERIMENTAL

The catalytical activity of the samples under study was measured in an integral flow reactor under the following conditions: reaction temperature 493·2 K, the molar ratio of the initial reaction mixture components $x^0(H_2O) : x^0(CO) : x^0(N_2) = 3 : 1 : 4$, pressure in the reactor $p = 0·103$ MPa. The catalytical beds were made by mixing 2 g of the catalyst of the grain size $0·08 — 0·1$ mm with 4 g of silica glass of the same grain size. In the measurements of the catalytical activity of precalcinated catalysts such amounts of the sample were used that correspond to 2 g of the catalyst in its commerical state (this approach was always used for samples that could not be calcinated directly in the reactor). The standard reduction conditions, the introduction of the catalyst into the reaction and its testing are described in detail in one of our previous papers[1]. The testing of the catalytical activity consisted of the measurement of the conversion degree $\alpha(CO)$ of carbon monoxide for various contact times τ. Water was removed from both initial and converted reaction mixtures and the contents of carbon monoxide and carbon dioxide were measured using the Orsat apparatus. Assuming that only the carbon monoxide conversion proceeds in the system, the conversion degree of CO must be given by Eq. (1)

$$\alpha(CO) = x(CO_2)/(x(CO) + x(CO_2)) = (1 - x(CO)/x^0(CO))/(1 + x(CO)) =$$
$$= (x(CO_2)/x^0(CO))/(1 - x(CO_2)) , \qquad (1)$$

where $x^0(CO)$ is the molar ratio of carbon monoxide in the initial mixture of $N_2 + CO$ and $x(i)$ is the molar ratio of the i-th component in the converted mixture (with water removed). The contact time τ was expressed by Eq. (2) in the time units ξ, defined as follows: if the reaction proceeds in the system at the temperature 473·15 K at the pressure of 0·103 MPa and at the catalyst loading 1 mole of CO/(hg), the contact time is exactly 1ξ. Therefore

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

where m is the catalyst weight in g and Q is the input of the $N_2 + CO$ mixture mol/h. The contact time changed within the limits $0·9 — 3\xi$, which correspond to the catalyst loading $2·15 — 0·63$ mole

of $CO/(hg)$. From the experimental dependences $\alpha(CO) = f(\tau)$ the reaction rate constants $k(\xi^{-1})$ were calculated assuming the validity of the kinetic equation $\alpha(CO) = 1 - \exp(-k\tau)$ (for more details, see ref.[1]).

In the first series of experiments the effect of calcination of the irradiated catalyst before reduction on the resulting radiation catalytical effect was studied. The irradiated sample was calcinated for 2 hours under the access of air at the chosen temperature, then the catalytical bed was prepared and the standard catalytical test[1] followed.

In the second series of experiments the dependence of the radiation catalytical effects on the calcination temperature of irradiated reduced catalysts was investigated using the following procedure: the irradiated catalyst, reduced by the standard method[1], was calcinated for 2 hours at the chosen temperature and under the flow of nitrogen directly in the reactor. The standard stabilization of the catalytical activity of the catalyst and testing of its activity followed.

In both series also analogous experiments with the unirradiated catalyst were made. The samples were irradiated by ^{60}Co γ radiation, by $^{90}Sr-^{90}Y$ β radiation, and by fast neutrons of the ^{252}Cf source. The irradiation methods and dose measurements are described in detail in the literature[1]. The treatment of samples began always 24—36 hours after irradiation, the absorbed doses were chosen so that they corresponded to the maximum of the radiation catalytical effects[1].

In the third series of experiments the effect of ^{60}Co γ radiation on the catalytical activity of the catalyst calcinated for 2 hours at 723·2 K under the access of air was studied. 2 g of the catalyst were calcinated, after the calcination the sample was irradiated by a chosen dose of radiation and the catalytical activity was measured by the standard test.

The relative catalytical activities C_{rel} and C_{rel}^0 were used for the comparison of the catalytical activities of the samples. They are defined by the Eqs (*3a,b*)

$$C_{rel} = k/k_{st} \quad C_{rel}^0 = k/k_{st}^+ , \qquad (3a,b)$$

where k is the rate constant of the reaction on the catalyst under test, k_{st} is the rate constant of the reaction catalyzed by the unirradiated catalyst introduced into the reaction by the standard procedure[1] (without calcination), and k_{st}^+ is the rate constant of the reaction proceeding on the catalyst, the history of which differs from that of the sample under test only in the fact that it was not irradiated. The values of C_{rel} characterize therefore the sum of the effects of thermal treatment and irradiation on its activity in the reaction, while the values of C_{rel}^0 are the measure of the radiation catalytical effect itself. From the definitions of both quantities it follows that for the catalysts irradiated in their commercial state and introduced into the reaction by the standard procedure[1] $C_{rel}^0 = C_{rel}$ and for the calcinated unirradiated catalysts $C_{rel}^0 = 1$. The use of relative catalytical activities makes possible a rather objective evaluation of the catalytical activity changes induced by the irradiation of the catalyst regardless of the observed changes of the catalytical activity of the unirradiated catalyst due to its calcination under the conditions given above.

RESULTS AND DISCUSSION

Table I (irradiated samples calcinated before reduction) and Table II (irradiated samples calcinated after reduction) present for comparison also the results of the catalytical activity tests of similarly irradiated samples that were not calcinated (exp. No. 9—11 in Table I and exp. No. 8—10 in Table II). The column "D, kGy" gives the values of absorbed doses together with the symbol of the applied radiation,

the column "T, K" gives the temperature of calcination, symbol "s" (standard treatment) is used for the non-calcinated samples. Table III summarizes the values of C_{rel} for the calcinated catalyst irradiated by different doses of γ radiation (column

TABLE I

Effect of calcination of the non-reduced irradiated catalysts on the radiation catalytical effect. Calcination conditions: 2 hours on air at the given temperature

Exp.	D, kGy	T, K	C_{rel}^0	C_{rel}
1	0	473·2	1	1·02 ± 0·06
2	0	623·2	1	1·08 ± 0·06
3	0	673·2	1	1·17 ± 0·07
4	0	723·2	1	1·09 ± 0·07
5	γ 380·8	623·2	1·11 ± 0·07	1·20 ± 0·07
6	γ 380·8	723·2	0·97 ± 0·06	1·06 ± 0·06
7	β 503·5	623·2	1·01 ± 0·07	1·09 ± 0·07
8	n_1^0 1·5	723·2	1·15 ± 0·07	1·25 ± 0·08
9	γ 380·8	s[a]	—	1·48 ± 0·07
10	β 503·5	s[a]	—	1·72 ± 0·09
11	n_1^0 1·5	s[a]	—	1·64 ± 0·08

[a] Non-calcinated catalysts.

TABLE II

Effect of calcination of the irradiated reduced catalysts on the radiation catalytical effect. Calcination conditions: 2 hours in the reactor under the flow of nitrogen at the given temperature

Exp.	D, kGy	T, K	C_{rel}^0	C_{rel}
1	0	673·2	1	0·89 ± 0·05
2	0	773·2	1	0·72 ± 0·04
3	γ 35·6	673·2	1·25 ± 0·07	1·11 ± 0·07
4	γ 35·6	773·2	1·06 ± 0·07	0·76 ± 0·05
5	β 62·9	673·2	1·09 ± 0·07	0·97 ± 0·06
6	β 62·9	773·2	0·97 ± 0·07	0·70 ± 0·05
7	n_1^0 1·14	773·2	1·29 ± 0·08	0·93 ± 0·06
8	γ 35·6	s[a]	—	1·52 ± 0·08
9	β 62·9	s[a]	—	1·80 ± 0·09
10	n_1^0 1·14	s[a]	—	1·70 ± 0·09

[a] Non-calcinated catalysts.

"calc.", the analogous values for the non-calcinated catalyst (column "s") are quoted for comparison.

From the results of Table I it is evident that the thermal pretreatment of non-reduced irradiated samples leads to a strong decrease or complete disappearance of the final radiation catalytical effect. From the values of C_{rel}^0 obtained by the comparison of irradiated and non-irradiated catalysts processed by the same thermal treatment it turns out that 2 hour calcination at 723·2 K causes a complete disappearance of the radiation catalytical effect induced by γ radiation (exp. No. 6), the same effect induced by β radiation disappears already at the calcination temperature of 623·2 K (exp. No. 7). A moderately higher catalytical activity survives in the γ irradiated sample calcinated at 623·2 K (exp. No. 5) and in the sample irradiated by fast neutrons and calcinated at 723·2 K (exp. No. 8). We can therefore conclude that the highest thermal stability of the radiation catalytical effect is observed for samples irradiated by fast neutrons and that this stability decreases in the sequence γ radiation − β radiation. This observation is in full agreement with the results of the time annealing of the radiation catalytical effects as described in our previous paper[2] and as it could be expected. The thermal treatment of irradiated samples under the access of air speeds up the annealing processes. These processes at the room temperature are reflected also by the observed dependence of the C_{rel} value on the time elapsed between the irradiation and the catalytical reaction. The differences in the temperature values, at which the radiation induced changes of the catalytical activity

TABLE III
Effect of γ radiation on the catalytical activity of precalcinated catalysts. Calcination conditions: 2 hours on air at 723·2 K

D, kGy	C_{rel}	
	calc.[a]	s[b]
0	1·09 + 0·06	1
0·4	1·07 ± 0·06	1·08 ± 0·06
1·5		1·19 ± 0·08
5·4	1·22 ± 0·05	1·33 ± 0·09
6·4	1·24 ± 0·07	
35·6		1·52 ± 0·08
50·2	1·22 ± 0·07	
380·8	1·23 ± 0·07	1·48 ± 0·07
1 483·6		1·51 ± 0·08

[a] Calcinated catalysts; [b] non-calcinated catalysts.

of samples are completely annealed, can be taken for a measure of the different stability of the precursors of the catalytically active centers modified or produced by different types of the ionizing radiation. Explanation of this different stability was proposed in the discussion of results of the time annealing of radiation catalytical effects[2].

Assuming that the charge defects formed by irradiation are responsible for the radiation catalytical effects, also the time and thermal stability of these charge defects could be directly correlated with the stability of the catalytical effects. The differences in the recombination kinetics of the primary charge defects induced by β and γ radiations are most probably connected with their different distribution in the irradiated material. The more homogeneous distribution of defects between the surface and bulk of the catalyst evidently contributes to the higher stability of the γ-induced radiation catalytical effects. Moreover, in the catalysts irradiated by fast neutrons that form a higher number of point or group defects than the β or γ radiations, the probability of the charge defects stabilization on these defects increases so that the neutron-induced radiation catalytical effects exhibit the highest stability.

From the values of C_{rel} in Table I (exp. No. 1—4) it follows that the precalcination leads to an increase of the catalytical activity of unirradiated samples. The maximum value of C_{rel} is achieved after calcination at 673·2 K (exp. No. 3). It has been proved by the X-ray diffraction[1] that the calcinated samples have a better crystalline structure of copper and zinc oxides and that an independent phase of $ZnO.Cr_2O_3$ is formed at higher calcination temperatures (773 K). The enhanced catalytical activity observed in the experiments Nos 2 and 3 (Table I) is evidently caused by the more perfect crystalline structure of zinc oxide that contributes to a higher dispersion of copper as the catalytically active component of the reduced catalyst. With the increasing dispersion of copper its resistance against sintering also increased as well as the selective surface of this component in spite of the fact that the total surface of the catalyst can decrease in a certain degree. The direct connection between the catalytical activity of this type of the catalysts $(CuO.ZnO.Cr_2O_3)$ and the area of the selective surface of copper has been proved in several studies[3−6] similarly as the connection between the dispersion and sintrability of copper on one hand and the perfect crystalline structure of zinc oxide on the other hand[4]. The enhancement of the catalytical activity of the $CuO.ZnO.Cr_2O_3$ conversion catalysts after precalcination was also described in the papers[3,7]. According to Saleta et al.[8] the catalyst material must be heated over 673 K to obtain a catalyst with a suitable conversion effectivity at 493 K. However, if the calcination temperature increases above a certain limit, the decrease of the total catalyst surface area becomes the dominant process and the catalytical activity will drop (exp. No. 4, Table I).

Table II shows that the values of the relative catalytical activity C_{rel} for irradiated catalysts calcinated after reduction are in all cases lower than the analogous values for catalysts introduced into the reaction by the standard procedure (exp. No. 8—10).

Evidently the fact that even the values of C_{rel} for an unirradiated catalyst decrease due to the calcination after reduction plays also a certain role in this case (exp. Nos 1 and 2, Table II). However, from the values of C_{rel}^0 it is evident that even in this case calcination leads to a decrease of the positive radiation catalytical effect. The enhanced catalytical activity in exp. Nos 4 and 5 does not seem convincing, in the exp. No. 6 (β radiation, calcination at 773·2 K) the enhanced catalytical activity was not observed. However, a significant effect is preserved in the sample irradiated by fast neutrons (exp. No. 7) even after calcination at 773·2 K. From the comparison of the results in Tables I and II it can be seen that due to the calcination of reduced samples the radiation catalytical effect evidently disappears in the γ irradiated catalyst, in the case of β irradiated catalyst it disappears very probably only at a higher calcination temperature if compared with the irradiated samples calcined in the non-reduced state. In the case of fast neutron irradiation a relatively higher radiation catalytical effect was observed in the experiment No. 7 (Table II) than in the experiment No. 8 (Table I). Further, it can be stated that the catalytical activity measured by the standard test is comparable for the catalysts of both series of experiments that were irradiated by the same type of radiation (exp. No. 9 − 11 of Table I and No. 8 − 10 of Table II). This fact means that the conceivable dependence between the magnitude of the primary radiation catalytical effect and the rate of its disappearance, or stability, from the point of view of the comparison of catalysts treated by the two thermal treatments and irradiated by the same type of radiation, is probably insignificant. From these facts it turns out that the calcination of reduced irradiated catalysts has a less pronounced influence on the final radiation catalytical effects than the calcination of the same samples before reduction. This is also in agreement with the experimental results that confirmed the time stability of the radiation catalytical effects of the conditioned catalyst kept under nitrogen atmosphere at the room temperature[2].

It can therefore be concluded that the radiation modified catalytically active centers are both time and thermally more stable system than the precursors, on the basis of which they are constituted during the reduction and conditioning of the catalyst. The dependences of C_{rel}^0 values on the type of the radiation applied and on the calcination temperature (Table II) show again the increase of the thermal stability of the radiation catalytical effects in the sequence β radiation − γ radiation − fast neutrons. Taking into account the results of experiments described in ref.[2] (time annealing studies) and the results discussed in this paper, it seems probable that there is a direct connection between the time and thermal stabilities of the precursors and the time and thermal stabilities of the catalytically active centers: The more stable radiation modified (formed) precursor gives a more stable radiation modified catalytical center. However, if the different properties of precursors modified by different types of radiation can be acceptably explained within the framework of the ideas discussed here or in the previous publications[1,2], the same model

can be hardly used in the case of the reduced catalyst. However, the different stability of the catalytically active centers modified by different types of radiation seems proved by the results of the second series of experiments and this fact is corroborated also by the long-term measurements of the catalytical activity of the irradiated samples as given in our previous paper[2]. Moreover, Table II shows that the values of C_{rel} decrease with the increasing temperature even for the unirradiated catalyst. The decrease of the catalytical activity is evidently caused by the sintering processes that proceed rather significantly under these conditions[3] and that are mainly responsible for the losses of the total surface area of the catalyst and also of the selective surface of copper[6]. This is borne out also by the fact that much lower values of the specific surface area were found for both catalysts in the experiments Nos 1 and 2 (Table II) than for the catalysts introduced into the reaction by the standard procedure.

The results of the γ radiation effects on the catalyst calcinated before irradiation at 723 K under the access of air are given in Table III, column "calc.". The value of C_{rel} increases with the increasing absorbed dose and at the dose of 5·4 kGy it reaches its limit value $C_{rel} = 1·22$ that is henceforth constant. Comparing this dependence with the analogous dependence for the catalyst that was not calcinated before irradiation (Table III, column "s") it is evident that both dependences have the same character, i.e., they are characterized by a "saturation" of the radiation catalytical effect. Moreover, we can see a significant difference in the achieved maximum effects; whereas in the case of the non-calcinated catalyst "saturation" corresponds to the increase of C_{rel} by about 50 per cent, this increase amounts only to 14 per cent in the case of the calcinated sample. It can be also seen that for the calcinated catalyst the "saturation" effect is achieved at lower absorbed doses (in the region of 0·4 − 5·4 kGy) than for the non-calcinated catalyst. It can therefore be concluded that from the point of view of the final radiation catalytical effect the non-calcinated catalyst is more sensitive than the calcinated one. The reason for this behaviour is then given by the fact that the final radiation catalytical effect is positively affected by the radiolysis of the not-fully-calcinated intermediates that are contained in the commercial catalyst and the presence of which was also proved by the X-ray diffraction[2]. Also the radiolytic products of water (either bound chemically or adsorbed from the air humidity) can manifest themselves in this respect. These processes have no effect (or much lower effect) in the case of the calcinated catalyst, the final radiation catalytical effect is lower and it is dominated by the interaction of the ionizing radiation with the system of oxides (or with the spinel $ZnO.Cr_2O_3$, respectively), that constitute the calcinated sample.

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