STUDY OF NICKEL-MOLYBDENUM CATALYSTS FOR METHANATION OF CARBON MONOXIDE

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Catalytic activity of nickel-molybdenum catalysts for methanation of carbon monoxide and hydrogen was studied by means of differential scanning calorimetry. The activity of $NiMoO_x$ systems exceeds that of carrier-free nickel if $x < 2$, and is conditioned by the oxidation degree of molybdenum, changing in dependence on the composition in the region Mo–MoO_2. The activity of the catalysts is adversely affected by irradiation by fast neutrons, dose 28·1 Gy, or by γ rays using doses in the region 0·8—52 kGy. The system is most susceptible to irradiation in the region of low concentrations of the minor component (about 1 mol.%). The dependence of changes in catalytic activity of γ-irradiated samples on the dose exhibits a maximum in the range of 2—5 kGy. The changes in catalytic activity are stimulated by the change of reactivity of the starting mixed oxides, leading to different kinetics of their reduction and modification of their adsorption properties. The irradiation of the catalysts results in lowered concentration of the active centres for the methanation reaction.

Catalytic synthesis of methane from hydrogen and carbon monoxide has been long studied. The increased interest in this reaction in the last years has brought a wealth of complex information concerning the reaction mechanism particularly on nickel catalysts[1-3]. More recent works have dealt with a detailed investigation of known catalysts as well as new systems with high catalytic activity and resistance to catalytic poisons. The methanation activity of molybdenum-containing catalysts has been so far studied almost exclusively with elemental molybdenum and molybdenum deposited on alumina[4]. In the present work, catalysts based on nickel and molybdenum and catalytic activity of the $NiMoO_x$ systems with different proportions of the two metals for the methanation reaction are studied.

EXPERIMENTAL

Nickel and molybdenum mixed oxides of different composition, whose preparation has been reported[5], were reduced in a differential scanning calorimeter Perkin–Elmer DSC-2. A sample, weight 2·00 ± 0·02 mg, was heated in a stream of dried and purified[6] hydrogen and carbon monoxide ($p(H_2) : p(CO) = 4$) from 450 to 700 K applying the rate of 20 K/min. After attaining the upper temperature limit, the sample was automatically cooled down to the starting temperature with the rate of 80 K/min. The gas flow rate was 100 ml/min for each chamber. The curve of dependence of the enthalpy change rate in the catalyst compartment on the temperature (methanation curve) was recorded on repeating the cycle. The zero line of the apparatus was obtained by executing the cycle with empty aluminium pans in identical conditions. The applicability and precision of the method have been verified experimentally[6]. The evolution of heat accompanying the catalytic synthesis of methane on the samples under study allowed the methanation to be monitored at temperatures higher than 450 K.

Portions of the starting mixed oxides were also γ-irradiated from a ^{60}Co source whose average dose power was 4·63 W/kg. The samples, sealed in polyethylene ampoules, were irradiated in this source by seven different doses covering the region of 0·8—52 kGy. In addition, irradiation by fast neutrons was also applied in an Amersham ^{252}Cf source containing 1 mg of Cf. The total absorbed dose was 28·1 Gy.

In order to increase the sensitivity of the method and reproducibility of measurements, the catalytic activity of the prior irradiated samples was compared with that of the corresponding unirradiated samples, by simultaneous measurement in the reference branch of the DSC. The differences between the two values were calculated from the difference of the records of two successive measurements, the samples in the two chambers being interchanged for the second measurement. All measurement parameters (flow rate of the synthesis gas 2 . 100 ml/min, $p(H_2)$: : $p(CO) = 4$, $p_{total} = 0·1$ MPa, apparatus setting) were maintained constant.

RESULTS

The obtained kinetic parameters of methanation are given in Table I. Obviously, in the case of samples with excess molybdenum (M 50 – M 100), the content of nickel

TABLE I

Catalytic Activity at 625 K (a_0) and Apparent Activation Energy of Methanation E_a on Nickel--Molybdenum Catalysts

Sample	Mo content wt.%	a_0 μmol s^{-1} g^{-1}	E_a kJ mol^{-1}
M 00	0·00	3·16	130 ± 5
M 01	0·89	24·6	188 ± 8
M 02	1·77	26·9	144 ± 7
M 05	5·02	186	106 ± 5
M 15	14·0	96·7	102 ± 6
M 30	29·3	57·5	105 ± 3
M 50	50·3	30·2	95 ± 3
M 70	71·0	18·7	95 ± 4
M 85	84·9	10·3	98 ± 2
M 95	94·3	3·89	106 ± 6
M 98	97·9	1·68	106 ± 5
M 99	99·1	1·02	76 ± 5
M 100	99·7	—	—

is decisive for the catalytic activity. As has been shown previously[5], in this composition region the molybdenum present is only reduced to Mo(IV), and MoO_2 acts as carrier for the finely dispersed nickel phase. Fig. 1 demonstrates a good agreement of the measured values of catalytic activity at 625 K with the values calculated assuming a constant activity of unit surface of elemental nickel, which is approximately $4{\cdot}2 . 10^{-7}$ mol/g s m^2 at the temperature applied. The partial specific surface area of nickel was determined based on X-ray structural measurements[5]. The behaviour of catalytic activity for the samples M 05 to M 100 (Table I), shown in Fig. 1, practically remains preserved within the whole temperature region examined, 450–700 K, in accordance with the common average value of apparent activation energy of methanation (Table I). The activation energy of the reaction is markedly enhanced in the samples M 00–M 02, where molybdenum represents the minor component.

The gamma as well as neutron irradiation resulted in a decrease in methanation activity of all catalysts. The temperature dependence of the catalytic activity difference exhibits first an exponential growth conforming to the Arrhenius' kinetic model (Fig. 2). The corresponding activation energy values for the reaction are identical with those determined for unirradiated samples. A result of irradiation of the starting oxides is a change in the frequency factor, the apparent activation energy of the reaction being not altered appreciably. In the region of high tempera-

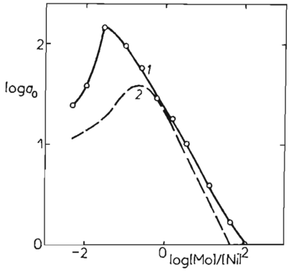

FIG. 1

Dependence of Catalytic Activity of the Samples on the Molybdenum-to-Nickel Concentration Ratio in Logarithmic Coordinates

1 Experimental data for 625 K; *2* theoretical dependence.

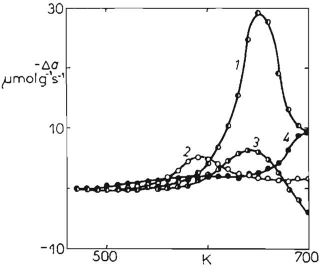

FIG. 2

Differences Between the Catalytic Activity of γ-Irradiated (D_γ = 10 kGy) and Unirradiated Samples as a Function of Temperature

Sample: *1* M 01, *2* M 30, *3* M 70, *4* M 00.

tures, where the reaction rate is controlled by diffusion, the difference between the methanation rates on irradiated and unirradiated samples decreases again. The flow rate of the reacting components is very high, so the reaction rate is probably governed by internal diffusion inside the catalyst pores. It can be thus inferred that the pore distribution in the irradiated samples is the same as in the unirradiated ones, only the density of the active centres for methanation on the former samples is lower. In the case of the sample M 100, which in the initial state was pure MoO_3, the temperature applied was only sufficient for reduction to molybdenum dioxide, which is inactive for methanation of carbon monoxide[4].

Fig. 3 shows how the catalytic activity change (Δa) of the sample M 01 γ-irradiated applying the dose of 6 kGy depends on the time elapsed since the end of exposition (t). The dependence found, which can be approximated by the relation $a = k \log t$ (where k is a constant), indicates that the catalytic activity is probably affected by the slow chemisorption of ionizable molecules on the surface of the initial semiconducting oxide occurring between the irradiation and the reduction by the synthesis gas[7]. The sorbate may be oxygen, which affects the reduction properties of the starting system as well as the catalytic properties of the reduced samples, and also water. The effect of the chemisorbed overstoichiometric oxygen of the starting oxides on the catalytic properties of the system after reduction could not be, however, proved, since the molybdenum trioxide present interfered with the iodometric determination of the ionogenic form of the overstoichiometric oxygen of NiO (refs[8,9]). Moreover, the content of the ionogenic chemisorbed oxygen in systems constituted by n- and p-semiconductors cannot be directly correlated with the adsorption properties of the systems[10]. In agreement with the results obtained by other authors[11], the content of chemisorbed oxygen was found to increase monotonically with growing dose applied.

The dependence of catalytic activity change on the dose of ionizing radiation exhibits a maximum in the range of 2–5 kGy for the whole composition region. The shape of this dependence for the samples M 00–M 02 is shown in Fig. 4. As can be seen from Fig. 5, demonstrating the dependence of the relative change in catalytic activity induced by neutron and gamma irradiation (dose 3·26 kGy) on the composition, in both cases the highest changes appeared with catalysts containing high excess of one component (samples M 01 and M 99). Pure nickel oxide, on the other hand, is rather insensitive to the transfer of the ionizing radiation energy to the final catalyst, and so are catalysts from the central part of the series.

DISCUSSION

The experimental data in conjunction with the analysis of the reduced catalysts[5] demonstrate that the methanation activity of $NiMoO_x$ system exceeds that of carrier-free nickel in case that $x < 2$. The positive effect of molybdenum appears starting from the lowest concentrations up to 29 wt.% MoO_3 (sample M 30). In this region, all molybdenum is reduced as far as the elemental state, and affects the structural parameters[5] – mean size of the crystallites, magnitude of the lattice parameter – of the major component (nickel) as well as its electronic state[12].

This effect is highest in the sample M 05, which exhibits the maximum catalytic activity (Table I), and decreases with decreasing nickel content in the system, the proportion of molybdenum reduced to the elemental state decreasing too. In the region of excess molybdenum, the catalytically active component is only nickel dispersed on the carrier, represented by lower valency molybdenum oxides[5] (MoO_2 and Mo_2O_3). This is evidenced by the values of apparent activation energy of the reaction (Table I), which are practically constant within a wide composition interval (M 01 – M 100), and also by the catalytic inactivity of molybdenum dioxide (reduced sample M 100). Only in the region of very low molybdenum concentrations in nickel is it feasible to assume direct interaction of the valence electrons of the two metals forming homogeneous solid solution, which is associated with a marked change in the activation energy.

The effect of molybdenum on the catalytic activity of nickel appears also in the attained degree of reduction of nickel oxide in the starting mixed system; it depends on the concentration and oxidation degree of the other component, and – owing to the higher affinity of molybdenum to oxygen – decreases with increasing content of molybdenum in the sample. As a result, in the region where nickel oxide is distinctly the major component, the catalytic activity rises with increasing content of molybdenum (Fig. 1). Analogous dependence of the methanation activity on composition, exhibiting a maximum, has been observed also by other authors[13] on multicomponent molybdenum catalysts, as well as the effect of degree of nickel oxide reduction on the activity of nickel catalyst[14]. Comparing the changes in the structural parameters of nickel in dependence on the catalyst composition[5] with the analogous dependence of the catalytic activity (Fig. 1), we can see that the positive effect of molybdenum on the catalytic properties of nickel can be directly correlated neither with the changes in the lattice parameters nor with the size of microcrystallites of elemental nickel.

The experimental results also reveal a negative effect of prior irradiation of the starting mixed oxides NiO–MoO_3 by γ-rays and fast neutrons on the activity of the final $NiMoO_x$ catalysts. The extent of this negative effect (lowering of the methanation rate) is function of the sample composition, and the radiation-induced change in activity depends not only on the absorbed γ-dose, but also on the time elapsed between the end of exposition and the reduction conversion of the oxide system to the catalytically active form.

The effect of ionizing radiation on the starting mixed oxides (interaction of *p*-semiconducting NiO with n-semiconducting MoO_3) is of complex nature. Gamma irradiation brings about first of all generation of nonequilibrium charge defects and, with higher doses and sufficient energy, rise in concentration of point lattice defects due to the bulk interaction within the crystal. Irradiation by fast neutrons results in formation of point defects or higher order defects (dislocations) which can also become new reaction centres. Charge defects are to a lesser extent induced also by secondary ionization processes. In addition, destruction of the existing surface centres[15] (polishing effect) can also occur. These processes may alter not only the reactivity of the solid phase, but also the adsorption capacity of the surface and the activation energy of chemisorption in dependence on composition. The changes in the adsorption properties are in accordance with the experimentally found growth of the content of the chemisorbed ionogenic oxygen, which affects directly the kinetics of reduction of nickel oxide[11] as well as of nickel oxide-containing binary mixed oxides[16]. Although a direct effect of chemisorbed oxygen of the starting oxides on the activity of the catalyst could not be proved, presumably because it is counterbalanced by the reduction, the increase of the catalytic activity with prolonged period between the end of the exposition and the start of the reduction (Fig. 3) evidences changes in the adsorption properties of both the starting system and the final catalyst. Recrystallization processes induced by the irradiation may play a part too. The change in reactivity of the irradiated mixed oxides appears in an altered kinetics of reduction as compared with the initial unirradiated samples[5]. Also, the apparent activation energy of reduction of samples prior irradiated by neutrons increased in the whole composition region in average by 28 kJ/mol as compared with the unirradiated mixed oxides.

The experimentally found change in catalytic activity on the irradiation of the starting systems indicates that all radiation-induced effects are relatively stable and the altered reactivity of the solid phase remains preserved after the reduction (memory effect in semiconductors[17]), when the system is changed chemically, the final catalyst being formed.

It can be thus assumed that the recovery of the radiation-induced defects (annealing) occurs only at the temperatures of reduction, and the reduction product will also exhibit different catalytic properties in comparison with the unirradiated sample owing to the different course, kinetics, and degree of reduction of the irradiated sample. The radiation-induced changes in catalytic activity in dependence on the absorbed dose and composition may result from processes occurring in the irradiated starting semiconducting oxides, and manifest themselves in the altered reactivity of the final catalyst's surface during its contact with the reacting gaseous components for the methanation.

The shape of dependence of the catalytic activity on the dose (Fig. 4) is due probably to two competitive processes: in the first stage the concentration of the active centres decreases (obviously because of the compensation of the positive charge in the nickel oxide acceptor band, which is the active component of the system), in the second stage new defects are generated on the surface, which appear as a consequence of the increasing defect concentration inside the crystal. This effect may be also accompanied by generation of new free charge carriers. Analogous shape of dependence of the catalytic activity on the absorbed dose of ionizing radiation of various kind, displaying a maximum, has been also observed with multicomponent copper-based hydrogenation catalysts[18], where the irradiated system was also converted to the

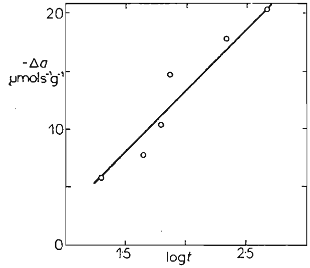

FIG. 3

Dependence of the Change of Catalytic Activity for the Sample M 01 on the Time Elapsed since the Irradiation by Dose D_γ = = 6 kGy

Reaction temperature 640 K; *t* time in hours.

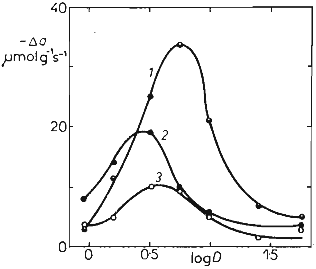

Fig. 4

Dependence of the Difference Between the Catalytic Activity of γ-Irradiated and Unirradiated Samples on the Dose

1 M 01, $T = 700$ K; 2 M 02, $T = 630$ K; *3* M 00, $T = 650$ K.

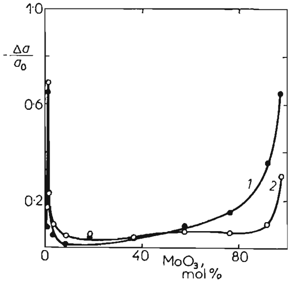

FIG. 5

Relative Changes in Catalytic Activity of γ-Irradiated Samples ($D_\gamma = 3{\cdot}26$ kGy) and Samples Irradiated by Fast Neutrons in Dependence on the Composition

Radiation: *1* neutrons, *2* gamma.

final active catalyst by reduction. No interpretation of such dependence has been so far suggested.

The radiation-induced relative change in catalytic activity, which is indicative of the sensitivity of the system to prior irradiation, exhibits pronounced maxima for samples with minimum concentration of the minor component (samples M 01 and M 99, Fig. 5). In this composition region, where the two components do not form separate crystal phases, the bonds of the minor component are affected most. The energy states are probably separated by high potential barriers, and thus are capable of stabilizing the charge defects stimulated by the ionizing radiation. In accordance with our previous results[10,16] we can assume in these samples the highest relative change in the degree of reduction of the catalytically active component (NiO), and hence also the highest change in the rate of the catalyzed reaction[14] and change in the reduction degree and valence states, of molybdenum as compared with the corresponding unirradiated samples. In the central part of the series, the mixed oxides involve in additional nickel molybdate phase[5] and thus possess a considerably more dense spectrum of energy levels, which brings about increasing probability of activated deexcitation of nonequilibrium states, associated with relatively fast recovery after irradiation. These samples are thus less susceptible to irradiation, and in accordance with experimental data, show smaller changes in catalytic activity than the samples on the two sides of the series except for pure nickel oxide and molybdenum trioxide.

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