CATALYST BASED ON NICKEL AND MOLYBDENUM OF A HIGH SPECIFIC SURFACE

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Reduction of mixed oxides NiO–MoO_3 of varying composition by hydrogen in the temperature range 653—773 K was studied as well as several physico-chemical parameters of the reduction products — methanation catalysts. Initial oxides contain — depending on their composition — a varying concentration of nickel molybdate as a free phase. The reduction of molybdenum oxide is catalytically influenced by nickel reduced and takes place, depending on its actual concentration, to the lower oxidation degrees eventually to the metallic molybdenum. On the other hand, the molybdenum present stabilizes nickel microcrystallites during the reduction by hydrogen. Resulting active catalytic systems exhibit a high specific surface. The rate, degree, and apparent activation energy of the reduction are markedly dependent on the initial sample composition. The reduction kinetics can be qualititatively described by an equation of the zone model of solid phase decomposition.

Reduction of molybdenum oxides has been widely studied during the last years, particularly in connection with the progress in powder metallurgy[1]. From the point of view of catalysis, attention has been paid to the reduction of molybdenum oxide without a carrier and to the effect of a carrier on its reduction kinetics and on its catalytic activity[2,3]. By a detailed study of the Mo–O system over the entire composition range MoO_3–Mo the existence of a series of phases corresponding to various oxidation degrees of molybdenum was proved[4]. The reduction of mixed oxides nickel–molybdenum, or nickel molybdate, is important because of the preparation of electrode materials, too[5]. However, properties of the reduced system have not been sufficiently studied so far, though they promise interesting information from the point of view of both heterogeneous catalysis and interaction between an easily and hardly reducible component of the system.

This communication reports on the results of a study concerning the dependence of several physico-chemical parameters of mixed oxides molybdenum–nickel and of their reduction products on the composition of the system.

EXPERIMENTAL

Initial substances of a series of mixed oxides of varying composition were nickel nitrate, molybdenum oxide, and ammonium hydroxide. All components were chemically pure. In the preparation of all samples equal volumes of a nickel nitrate solution neutralized by ammonia and of an ammoniacal solution of ammonium molybdate of pH 11 ± 1 were mixed. The mixture was concentrated by evaporation to a paste at 345—370 K and then dried twice for six hours at 380 K. The products were calcinated on air for two hours at 700 K.

With the calcinated systems specific surfaces were measured by nitrogen at low temperatures. Their fine structure was determined by the Bragg-Brentano method using a lamp with a copper cathode. The nickel content was obtained by the complexometric method, molybdenum was determined by polarography. Initial samples were reduced by a nitrogen-hydrogen mixture ($p(H_2)/$ $/p(N_2) = 6$) at 710 K. The course of the reduction was followed by the thermal conductivity detection of hydrogen concentration changes in the flowing reducing mixture. The reduction was stopped in several stages of the process and the specific surface of reduction intermediate pruducts was measured. The corresponding reduction degree α_t was calculated from

$$\alpha_t = S_t \alpha_\infty / S_\infty , \tag{1}$$

where S_t is the reduction peak area from the start to time t, S_∞ is the similar quantity after 2 hour reduction. The overall achieved reduction degree α_∞ was determined from the mass loss during the reduction.

After two hours the reduction rate decreased below a measurable value. The specific surfaces corresponding to this reduction degree are summarized in Table I as the values of the reduced systems. Kinetic parameters of the reduction of mixed oxides by hydrogen over the temperature range 653—773 K were measured separately using an earlier described thermogravimetric apparatus[6]. The apparent activation energy of reduction E_a was calculated using the Arrhenius equation from values of rate constants k which fit the equation

$$1 - (1 - \alpha)^{1/3} = kt . \tag{2}$$

The values of E_a, namely with samples containing an excess of molybdenum, have been calculated from measurements over a narrow temperature interval — in view of the relatively high reduction temperatures — and exhibit thus a fairly high inaccuracy (relative error up to 20%).

RESULTS AND DISCUSSION

The calcinated systems contain over a wide composition interval (samples M 30 to M 95) besides the oxides of both metals, NiO and MoO_3, also a separate phase of crystalline nickel molybdate. Its presence was proved by the occurrence of characteristic selective reflections in X-ray diffractograms of the above mentioned samples. The results in Table I indicate a high degree of mutual influence of the basic components of the system. The dependence of the specific surfaces on the composition exhibits a maximum for both the initial and reduced samples. In the former case, the position of the maximum does not coincide with the maximum of the nickel molybdate concentration which may be assumed to occur in samples around the series center (a comparable abundance of Mo and Ni). Neither does the maximum position correspond to a simple superposition of the specific surfaces of the particular components. The observed specific surface changes (their dependence on the reduction degree is shown in Fig. 1) and the maximum values of the reduced sample surfaces (samples M 50 and M 70, Table I) evidently hang together with reaching during the reduction the mean valence of Mo corresponding to the oxide of the stoechiometry

Mo_2O_3. This finding is in agreement with results of several authors[2] who report from redox titration determinations a mean valence of molybdenum 3·5 for the reduction product of MoO_3 of the maximum specific surface. On the contrary, other authors[7,8] argue that the formation of Mo_2O_3 during the MoO_3 reduction is improbable. X-Ray studies of reduced samples showed the presence of elementary nickel in all samples up to M 70. Starting with the mixed oxide M 30, selective reflections can be detected in the system which evidently correspond to the oxides Mo_2O_3 and MoO_2. Though their exact identification and mutual differentiation based on the published data[9] is not unambiguous, it is in full agreement with the results in Table I, where the value of Mo mean valence was calculated from thermogravimetric data. A microstructural proof of the separated phase of elementary molybdenum or of a possible intermetallic phase of both metals (Ni_4Mo) was not positive – mainly because of a low concentration of the sought phases. However, the value of the lattice parameter of nickel depends strongly on the molybdenum content in the system, as can be seen from Fig. 2. This dependence may be interpreted, in agreement with the other results, in the following way: with samples of a low molybdenum content (M 01 up to M O5) reduction of molybdenum oxide to the metal takes place, and with the in-

TABLE I

Designation, Composition, Specific Surfaces of Initial Oxides and Reduced Samples and Final Mean Valence of Mo after Reduction

Sample	NiO weight %	MoO_3 weight %	MoO_3 mol %	S_{init} $m^2 g^{-1}$	S_{red} $m^2 g^{-1}$	Valence of Mo
M 00	98·72	0	0	8·8	1·61	—
M 01	97·62	0·89	0·47	5·4	2·85	0
M 02	96·70	1·77	0·94	3·6	5·69	0
M 05	93·99	5·02	2·71	35·7	7·5	0
M 15	84·82	14·0	7·90	41·1	52·7	0
M 30	68·86	29·3	18·1	46·2	126	2·3
M 50	48·42	50·3	36·1	17·5	246	3·1
M 70	27·28	71·0	57·5	19·8	232	3·0
M 85	13·81	84·9	76·2	7·5	69·8	4·4
M 95	4·18	94·3	92·2	4·2	28·5	3·8
M 98	1·26	97·9	97·6	2·49	11·1	3·9
M 99	0·62	99·1	98·9	2·31	7·61	4·1
M 100	0	99·7	100	2·24	2·35	3·9

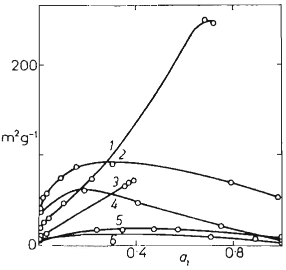

FIG. 1

Dependence of Specific Surfaces of Samples S on the Reduction Degree α_t

1 M 50, *2* M 15, *3* M 85, *4* M 05, *5* M 02, *6* M 01.

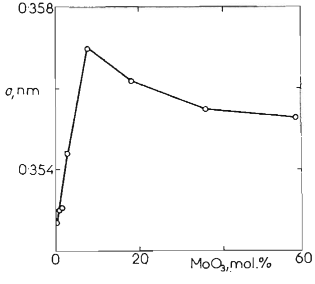

FIG. 2

Dependence of Ni Lattice parameter on the Composition

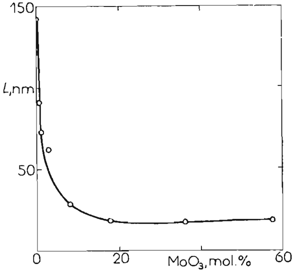

FIG. 3.

Dependence of the Size of Ni Coherent Regions L on the Sample Composition

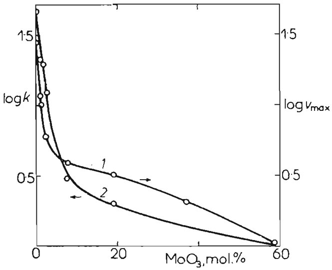

FIG. 4.

Dependence of the Logarithm of the Reduction Rate Constant (*2*) and of the Maximum Reduction Rate (*1*) on the Composition

Reduction temperature 653 K.

creasing molybdenum content the lattice parameter of nickel increases. Thus nickel catalytically influences and facilitates reduction of molybdenum oxide to lower oxidation stages. From a certain composition on (M 05) the actual nickel concentration is not sufficient to influence the reduction of all molybdenum to the metal and thus its concentration decreases with the increasing nickel concentration. At the same time, a partial restoration of the original lattice parameter of nickel takes place (Fig. 2). On the contrary, molybdenum oxides influence the nickel oxide reduction and stabilize microcrystallites of nickel. The dependence of the size of coherent zones of nickel on the system composition is shown in Fig. 3. The observed dependence of the degree and rate of reduction on the composition of the system agrees with this described mechanism of mutual interaction of both components. With samples of a low molybdenum content (up to approximately M15) the degree of reduction of the system – calculated under the assumption of the total reduction of both oxides to metals – is practically equal to unity at 710 K and decreases with the increasing molybdenum content. Fig. 4 illustrates the dependence of the logarithm of the rate constant and of the maximum reduction rate on the composition of the system. It follows from this figure that these quantities drastically decrease with the increasing MoO_3 content in the initial system. Also, the apparent activation energy of reduction depends strongly on the composition. The dependence of the activation energy on the relative abundance of both metals can be expressed as

$$E_a = A \log (n_{Mo}/n_{Ni}) + B \,, \tag{3}$$

where n_{Mo} and n_{Ni} are molar % of the respective metals in the samples; the values of the constants are: $A = 105$ kJ/mol, $B = 210$ kJ/mol.

The reduction yields catalytically active systems for the synthesis of methane from hydrogen and carbon monoxide. Their activity in this reaction is the subject of a forthcoming study.

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