JOURNAL OF MATERIALS SCIENCE 28 (1993) 1937–1940

Porous materials sintering under conditions of catalytic reaction

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The effect of exothermal catalytic reaction of oxidation of carbon monoxide upon the strength and porosity of iron and nickel catalysts was analysed. It has been shown that during the course of this reaction at 573–623 K, a substantial four- to six-fold increase in the strength of the above catalysts occurs (under fixed porosity) if compared to samples annealed under the same temperature in an inert medium or in the presence of one of the components of the reaction. This effect is caused by facilitation of surface self-diffusion due to catalysis, and permits essential reduction of the sintering temperature. Similar effects have been observed on oxide (MgO, V_2O_5) catalysts.

1. Introduction

In previous studies the method of single-scratch "healing" [1, 2] was used to show that the heterogeneous catalytic exothermal reactions (under isothermal conditions) may result in abrupt (by four or five orders of magnitude) increase in the coefficient of surface self-diffusion, $D_{s,c}$, if compared to the value of D_s obtained at the same temperature but in the absence of catalysis. These results were observed in reactions of ammonium synthesis from a nitrogen-hydrogen mixture (823 K) and hydrogenation of benzene (373 K) upon compact crystalline samples of iron and nickel, respectively. The results obtained fit the concepts developed in our previous studies concerning the reciprocal effects of solid bodies and the reaction medium during heterogeneous catalysis [3, 4].

Because the effect was absent in an endothermal reaction involving the same type of catalyst (the dehydrogenation of cyclohexane), the increasing value of $D_{s,c}$ during catalysis might be naturally related to the thermal effect of the reaction. A suggestion was put forward that the energy released in each catalytic act is mainly (or completely) spent not upon the heating of the catalyst but rather used locally in the surface layer of the solid body to break bonds between atoms (ions) on which or close to which the catalytic act occurs. This energy might be used in tearing the separate atoms from the lattice (particularly from a surface area with a high curvature) and their transition into the state of absorbed atoms (adatoms). Because the absolute value of the thermal effect per mole of the reactions studied is two to three times as much as the energy necessary to create one mole of adatoms iron and nickel, one could expect that each act may result in up to two or three additional adatoms participating in self-diffusion surface mass transfer.

Owing to the increase in $D_{s,c}$ during the catalytic reaction one might also expect a decrease in the sintering temperature, ΔT, of the particles and, consequently, an increase in the strength of the porous structure of compressed powdered catalysts, when compared to the strength of similar samples annealed at the temperature of the catalytic reaction but in an inert medium [5]. Because the heterogeneous catalytic reaction develops only upon the surface of a solid body (catalyst) it is logical to expect that such an increase in strength will be caused due to the increasing area of the true contacts between the particles while retaining the porosity of the samples fixed.

Naturally, the above effect of increasing strength of catalysts in exothermal reaction can be detected only when it is greater than the effect of adsorption decrease of the strength of the related porous structure, as shown earlier [6, 7], with facilitation of the rupture of the most strained bonds between atoms (ions) in contacts within the porous structure due to adsorption (chemisorption) of the components of the medium, including intermediate products.

To verify these suggestions, we examined the effect of the highly exothermal reaction of the oxidation of carbon monoxide ($\Delta Q \sim 250$ kJ mol^{-1}) while varying

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the strength and porosity of the samples catalysing this réaction (disperse porous iron and nickel samples).

The catalysis was carried out in a through-put installation under atmospheric pressure at isothermal conditions; the catalyst's temperature was increased during the reaction by no more than 0.2° C. The reacting gases (oxygen and carbon monoxide) entered the reactor in a mixture with helium. As a rule, the partial pressures of reagents corresponded to stoichiometry of CO oxidation. We varied the temperature, exposure time and the rate of through-put of the gas mixture. The annealing of control samples was realized in an atmosphere of inert gas (argon or helium) under the same temperatures and exposure times as those observed during catalysis. We also elucidated the effects of various components of the reaction: CO (mixed with helium) and O_2 (in air) and those of H_2 upon the strength of catalyst samples.

2. Experimental procedure

The catalysts were prepared as cylindrical tablets ($h = d = 0.5$ cm) by compressing powdered carbonile iron and electrolytic nickel. The powders were composed of particles of approximately fixed size ($1–3 \times 10^{-3}$ cm) and differed only in the shape of particles: the iron particles were spherical whereas those of nickel were elliptical. The ethanol was added to the powder during pressing to obtain samples with a controlled density (and consequently, strength) at minimum pressures (~30 MPa). After compression, the samples were annealed for 2 h at 473 K (Fe) and 573 K (Ni).

The conditions for sample preparation described resulted in decreasing residual internal stresses; it was important to increase the effect of strengthening and to eliminate the possible manifestation of the opposite effect of an adsorption-induced decrease in the strength. We determined the strength of the samples under uniaxial compression, and their overall porosity. The data on the size of particles and contacts between them were obtained by SEM.

The strength of the samples was not examined under the influence of the medium, but when the samples were removed from reactor. Owing to this, the fraction of adsorption-induced decrease in the strength, which was caused by the weakening of interatomic bonds only when in contact with the medium, essentially did not influence the detection of the strengthening effect. The effect of irreversible rupture of the bonds (the most strained ones) was minimized through the use of soft preparation conditions followed by annealing of the catalyst samples.

3. Results and discussion

Table I shows the variation in strength of samples of carbonile iron after their annealing in various media. It is seen that during catalysis (under 573 and 623 K), an abrupt (by four to five times) increase in the strength of samples was observed compared to that of the control or that annealed in the presence of one of the reaction components. At the same time, the electron micrographs revealed the development of contacts during annealing of the samples under conditions of catalytic reaction. In the absence of a reaction (at a fixed temperature) this effect is less pronounced. Because neither the size of particles nor the porosity of the samples varied under these conditions (within experimental error ~0.1%) the increase in strength may be related to the increasing contact area between particles of the porous structure, due to the facilitated diffusion of adatoms into the contact zone.

TABLE I The strength, P, of iron catalyst after catalysis (oxidation CO) and annealing in various media for 30 min

Composition of reactants	P (MPa)	
	573 K	623 K
8% CO + 4% O_2 + 88% He (Catalysis)	6.5	7.4
Air	2.4	2.9
Argon	1.4	1.5
8% CO + 92% He	0.3	0.4
H_2	–	0.9

Note: the rate of through-put of reactants = 100 ml $\min^{-1}$; the strength of initial samples = 1.3 MPa; porosity of samples 57.5%.

TABLE II The effect of duration of catalysis and of the rate of through-put of the reaction medium (2% CO + 1% O_2 + 97% He) on the strength, P, of samples of iron

Through-put rate (ml $\min^{-1}$)	P (MPa) at		
	5 min	15 min	30 min
50	–	3.1	–
100	3.0	3.5	6.5
200	–	4.7	–

Note: the strength of control samples = 1.2 MPa; porosity of samples 62.0%; temperature 623 K.

It was also established experimentally (Table II) that the strengthening of iron samples increased with increasing duration of the catalytic reaction (over the interval 5–30 min) and for a reactant through-put rate (of 50–200 ml $\min^{-1}$), i.e. it depends on the overall number of catalytic acts developing upon the catalyst surface. Fig. 1 shows a log–log plot of the dependence of the strength of samples of iron catalysts, P, as a function of duration, τ, of sintering during catalysis. The slope of the straight line obtained with these coordinates enables one to determine the coefficient, n, in the equation of sintering kinetics: $x \infty \tau^{1/n}$, where x is the diameter of the contact zone between particles. Indeed, at fixed porosity $P \infty x^2$; consequently, $P \infty \tau^{2/n}$, and $\lg P = 2/n \lg\tau + \text{const}$.

In the case of sintering of particles resulting from the mechanism of surface self-diffusion, the theory predicts the value $n = 7$ or 6 depending on the roughness of the particles (7 for smooth particles, and 6 for rough ones). The value $n = 6.4$ obtained from Fig. 1 indicates that the strengthening caused by the growing contact area between the particles occurs due to the surface self-diffusion.

It should be noted (Table I) that during heating of iron samples in the presence of only one of the reaction components (CO or O_2) and in hydrogen, the strength compared to the control samples becomes higher in oxidation (air) and lower in reduction (CO and H_2) media (at fixed porosity). These moderate effects are, presumably, caused by some variations of the apparent contact area due to the appearance (increasing strength) and disappearance (decreasing strength) of oxide bridges in the respective media during annealing.

An abrupt strengthening of the catalyst at fixed porosity was obtained in the same reaction using samples of electrolytic nickel. Thus, the strength of the nickel catalyst after 60 min catalysis at 623 K was six times higher than the strength of control samples annealed at the same temperature and exposure time in a helium atmosphere.

It is especially interesting to evaluate the decrease in the sintering temperature, ΔT, due to the catalytic reaction. The strengthening of porous structures of iron and nickel in an inert medium similar to that obtained in the catalytic process was observed only at temperature differences exceeding 300–350 °C (this was always accompanied by a marked shrinkage of samples and a decrease in their porosity). Hence, under conditions of the catalytic reaction, the sintering temperature of the metal powders studied sharply decreased due to acceleration of surface diffusion mass transfer only (under elevated temperatures the annealing accelerates both the surface and volume diffusion). Using the well-known relationships between the surface self-diffusion coefficient, D_s, and the temperature, T [8], we may write

$$D_s = D_0 e^{-U/kT} \tag{1}$$

where U is the activation energy of the surface self-diffusion of atoms. Let us estimate at what temperature, T', the value of D'_s in an inert medium coincides with the value $D_{s,c}$ obtained when the catalysis develops at the temperature T_c. We arrive at the following equation

$$\frac{D_{s,c}}{D_s} = \frac{D'_s}{D_s} = \exp[U(T' - T_c)/kT'T_c] \tag{2}$$

hence

$$T' = \frac{T_c}{\left(1 - \frac{kT_c}{U}\ln\frac{D_{s,c}}{D_s}\right)} \tag{3}$$

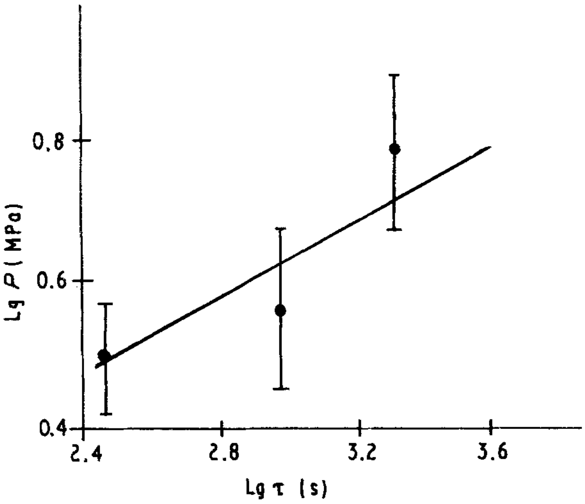

Figure 1 The strength, P, of samples of iron catalysts plotted as a function of duration, τ, of the developing catalytic reaction.

Table III lists results of calculations made using Equation 3 for the ratio $D_{s,c}/D_s = 10^5$ which, as mentioned above, was obtained for iron and nickel catalysts in experiments on scratch "healing" (in exothermal reactions having close values of thermal effect). The values of activation energy of the surface diffusion for iron and nickel were taken from [8]. As the data given in Table III suggest, the calculated values $\Delta T = (T' - T_c)$ are close to the experimental values $\Delta T \sim 300$–350 °C.

Therefore, these experiments indicate that under conditions of exothermal catalytic reaction, the sintering temperature of metal powders substantially decreases. Under these conditions the pronounced strengthening of porous structures due to development of contacts between the particles takes place while retaining the initial porosity, which is important both for catalysts and adsorbents, and for membranes.

It has been established that this effect also takes place for powders of oxides. The influence of an exothermal reaction (ethanol oxidation) on the strength of MgO and V_2O_5 catalysts has been studied at 670 and 450–570 K respectively. Samples were prepared by pressing; their strength (measured after catalysis) was compared with that of similar samples annealed at the same temperature in the absence of reaction.

In the first stage (up to 30 min), no essential changes in strength were observed; probably the increase in strength due to sintering was compensated

TABLE III The sintering temperature under conditions of catalysis (T_c) and in an inert medium (T') ensuring the formation of similar contacts between particles

Catalyst	U (kJ mol^{-1})	T_c (K)	T' (K)	$\Delta T = T' - T_c$ (K)	ΔT_{exp} (K)
Ni	198.6	623	888	265	300–350
Fe	176.0	623	941	318	

partially, or even fully at the expense of an adsorption-induced decrease in strength, depending upon the conditions of sample preparation (oxide dispersity, temperature of $Mg(OH)_2$ dehydration, pressure). However, after 2–4 h catalysis, a reproducible effect, 25%–50% increase in sample strength, has been observed. It is essentially less pronounced compared with metals, possibly because of high defectiveness (initial metastability) of the oxide powders used. It should be noted that the same moderate strengthening of V_2O_5 samples when annealed in air is reached only at a temperature about 80% of the melting point.

In conclusion, it should be stressed that the use of catalysis to decrease the sintering temperature might be important for substances undergoing phase transition (e.g. decomposition) under "usual" sintering temperatures.

Acknowledgements

This research project was formulated and was begun under supervision of the late Ya. E. Geguzin. L. N. Sokolova is thanked for participation in experiments with MgO and V_2O_5. The authors thank Dr A. Westwood, Professor R. Green, Dr S. Friedman, Dr B. Yakobson, Professor J. Hren, Professor H. Palmour, and Professor G. Roberts for useful discussions.

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Received 20 May
and accepted 30 June 1992