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ScienceDirect
Mendeleev Commun., 1991, **1**(**4**), 136–137

Mendeleev
Communications

Sintering of Metallic Porous Samples under the Conditions of a Catalytic Reaction

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The influence of the exothermic catalytic reaction of oxidation of carbon monoxide upon the mechanical strength and porosity of iron and nickel catalysts has been analysed and it has been shown that in the course of this reaction a decrease in the sintering temperature occurs which results in a 4–6-fold increase in the strength of the catalysts (at a given porosity) compared with that of control samples.

Previous studies[1,2] have shown that heterogeneous exothermic catalytic reactions result in an abrupt increase (10^{4-5}) in the coefficient of surface self-diffusion ($D_{\mathrm{S},C}$) compared with the value of D_{S} obtained at the same temperature but in the absence of catalysis. These results were obtained for ammonia synthesis (823 K) and benzene hydration (373 K) reactions on polycrystalline iron and nickel, respectively.

It was suggested that the energy released in each catalytic act is spent not upon heating the catalyst but, rather, is used locally to break bonds between separate atoms (ions) in the surface layer of the solid body (upon which or close to which the catalytic act occurs). This energy may be used to 'tear' separate atoms from the lattice, *e.g.* from surface cracks, and their transition into the adsorbed atoms state (adatoms). Since the absolute value per mole of the thermal effect of the reactions studied is 2–3 times the energy necessary to create 1 mole of adatoms of Fe or Ni one might expect that each act results in up to 2–3 additional adatoms participating in surface diffusion mass transfer.

Owing to the increase of $D_{\mathrm{S},C}$ in the course of a catalytic reaction one might also expect a decrease in the temperature ΔT of sintering (baking) of particles and, consequently, an increase in the mechanical strength of the porous structure of compressed powdered catalysts compared with that of similar samples annealed at the temperature of the catalytic reaction but in inert media. Since a heterogeneous catalytic reaction develops only upon the surface of a solid body – the catalyst – it follows that such an increase in strength is due to an increase in the area of true contact between particles while a fixed porosity of the samples is retained.

Naturally, the above effect of increased strength of a catalyst during an exothermal reaction can be detected only when it is greater than the effect of adsorption in decreasing the strength of the porous structure. This is related, as shown earlier,[3–5] to the facilitation of cleavage of the most strained bonds between atoms (ions) in contact within the porous structure due to adsorption (chemisorption) of the components of the medium, including intermediate products.

In order to verify these suggestions we examined the effect of the highly exothermal carbon monoxide oxidation ($\Delta Q = 250$ kJ mol^{-1}) on the strength and porosity of the samples catalysing this reaction: disperse porous iron and nickel samples.

The reaction was carried out in a flow system at atmospheric pressure under isothermal conditions. The temperature of the catalyst was increased during the course of the reaction by no more than 0.2 °C. The reacting gases, oxygen and carbon monoxide, entered the reactor mixed with helium. As a rule, the pressure of the reagents corresponded to the stoichiometry of CO oxidation. We varied the temperature, exposure time and the rate of throughput of the gas mixture. Annealing of control samples was performed in an atmosphere of inert gas (argon or helium) using the same temperatures and exposure times as those for the catalytic system. We also elucidated the effects of the various reaction components: CO (mixed with helium), O_2 (in air) and H_2 upon the strength of the catalyst samples.

The catalysts were prepared as cylindrical tablets ($h = d = 0.5$ cm) by compressing powdered iron [obtained from Fe $(CO)_8$ and electrolytic nickel. The powders were composed of particles of approximately equal size (1–3 μm), differing only in their shape: the iron particles were spherical whereas those of nickel had an elliptical shape. During compression ethanol was added to the powder in order to obtain samples having the desired 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 of sample preparation described resulted in reduced residual internal tension which, as this had been proposed to correspond with the adsorption-induced decrease in strength was an important condition to enhance the effect of increased strength.[3]

In the course of experiments we determined the strength of the samples with respect to compression (in an axial direction) and their overall porosity. Data on the size of particles and the contacts between them was obtained by reflection electron microscopy (REM). The sample strengths were not examined *in situ*, but after extraction of the samples from the reactor. The fraction of adsorption decrease in strength caused by the weakening of interatomic (interionic) bonds is thus manifested only when the medium influences the detection of the strengthening effect. The effect of irreversible cleavage of these bonds (the most strained ones) was minimized by the use of mild compression conditions, followed by annealing of the catalyst samples.

Table 1 lists the variation in strength of samples of iron carbonyl after annealing in various media. These results show an abrupt growth (4–5 times) in the strength of the samples during the catalytic process (at 573 and 623 K) compared with that of control samples annealed in the presence of one of the reaction components. At the same time electron microscopic photographs of the Fe particles revealed the contacts formed during the annealing of samples under the conditions of the catalytic reaction. In the absence of the reaction (at a fixed

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Table 1 Strength P of iron catalyst after catalysis (oxidation of CO) and annealing in various media for 30 min[a]

	P/MPa	
	Temp./K	
Composition of reactants	573	623
8% CO + 4% O + 88% He (catalyst)	6.5	7.4
Air	2.4	2.9
Ar	1.4	1.5
8% CO + 92% He	0.3	0.4
Hz	—	0.9

[a]Rate of throughput of reactants 100 ml min^{-1}, strength of initial samples 1.3 MPa, porosity of samples 57.5%.

temperature) this effect is less pronounced. Since neither the particle size nor the porosity of samples varied under these conditions (within experimental error ± 0.1%), the growth in strength may be related to the increased contact area between the particles of the porous structure, facilitating the diffusion of adatoms into the contact zone.

It was also established experimentally (Table 2) that the effect of strengthening the iron samples increases with the duration of the catalytic reaction (over the interval 5–30 min) and the rate of reactant throughput (50–200 ml min^{-1}), *i.e.* it depends on the overall number of catalytic acts developing upon the catalyst surface.

It should be noted (Table 1) that on heating iron samples in the presence of only one reaction component (CO or O_2) or in hydrogen the strength, if compared with those the control samples, become higher in oxidising (air) and lower in reducing (CO and H_2) media (the porosity being fixed). These effects are, presumably, caused by variation of the apparent contact area due to cleavage (decreasing strength) and formation (increasing strength) of oxide 'bridges' in the respective media during annealing.

A sharp increase in strength 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 6 times higher than that of control samples annealed at the same temperature and exposure time in helium.

Table 2 Effect of duration of catalysis and of the rate of throughput of reaction medium (2% CO + 1% O_2 + 97% He) on the strength P of iron samples[a]

	P/MPa		
	Time/min		
Throughput rate/ml min^{-1}	5	15	30
50	–	3.1	–
100	3.0	3.5	6.5
200	–	4.7	–

[a] Porosity of samples 62.0%, strength of control samples 1.2 MPa, temperature 623 K.

Table 3 Sintering temperature under catalysis conditions (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	ΔT
Ni	198.6	623	888	265
Fe	176.0	623	941	318

It was interesting to establish experimentally such a decrease in the sintering temperature ΔT, ensuring the development of the catalytic reaction. Strengthening of the porous structures of iron and nickel catalysts in inert media, similar to that observed in the catalytic process, was observed only at temperatures exceeding 300–350°C (this was always accompanied by a marked shrinking of samples and by a decrease in their porosity). Hence, under conditions of exothermal reaction the sintering temperature of the metal powders studied sharply decreased, resulting in acceleration of surface diffusion mass transfer only (at elevated temperatures annealing accelerates both surface and volume diffusion). Using the well-known relationships between D and temperature T[6] we may write eqn. (1),

$$D_S = D_0 e^{-U/kT} \qquad (1)$$

where U is the activation energy for surface self-diffusion of atoms. In estimating temperature T' at which the value of D'_S in an inert medium coincides with the value $D_{S,C}$ obtained when catalysis develops at a temperature T_C, we arrive at eqn. (2)

$$\frac{D_{S,C}}{D_S} = \frac{D'_{S,C}}{D_S} = \exp\{U(T' - T)/kT_CT'\} \qquad (2)$$

whence

$$T' = \frac{T_C}{1 - \left(\frac{kT_C}{U}\right)\ln\left(\frac{D_{S,C}}{D_S}\right)} \qquad (3)$$

Table 3 lists the results of calculations made using eqn. (3) for the ratio $D_{S,C}/D_S = 10^5$ which, as mentioned above, was obtained for Fe and Ni catalysts in experiments on scratch 'healing' (in exothermal reactions having close values of thermal effect). The values of the activation energy for surface diffusion for Fe and Ni were taken from ref. 6. As shown in Table 3, the calculated values $\Delta T = (T' - T_C)$ are close to the experimental values ΔT.

Therefore, these experiments indicate that under the conditions of catalytic exothermic reactions the sintering temperature of metal powders substantially decreases. Under these conditions there is a pronounced strengthening of the porous structures due to the development of contacts between particles while the initial porosity, which is important both for catalysts and adsorbants and for membranes. The use of catalysis to decrease the sintering temperature could be extremely important for substances undergoing phase transitions (*e.g.* decomposition) at their 'usual' sintering temperatures.

We gratefully acknowledge the contribution of Ya. E. Geguzin, who took part in formulating this research project. He was held in the highest regard by all who met and worked with him.

Received in USSR, 12th April 1991
Received in UK, 12th June 1991; Com. 1/01919H

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