The Effect of the Temperature on the Fluidization of Supported Metal Catalysts

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The fluidization technique has become a widely-used method for solid-gas contact operations in the chemical industry. In general, metal powder shows agglomeration when it is heated in a hydrogen stream.[1,2] In hydrogenation experiments using a fluidized bed appearatus, it is necessary to find a metal powder catalyst which is stable without agglomeration under the reaction conditions. The aim of the present experiments is to find such a catalyst, on which shows stable fluidization characteristics under the operating conditions.

Experimental Method

Metal Powders for the Fluidization Experiments.—Commercial-grade metal powders of silver, copper, nickel, iron and stainless steel were used.

The Preparation of Supported Nickel and Cobalt Catalysts for the Fluidization Experiment.—30% *Nickel-Diatomaceous Earth.*—Powdered diatomaceous earth was added to a solution of a 1 N nickel nitrate solution to the slurry; then these was slowly added, at 20°C, an equivalent quantity of ammonium carbonate dissolved in water. The precipitate, after being filtrated and washed, was dried at 100°C and calcined at 400°C for 2 hr.

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1) E. Echigoya and G. L. Osberg, *Can. J. Chem. Eng.*, **38**, 43 (1960).

2) E. Echigoya presented in part at 2nd Meeting of Chemical Reaction Eng. Osaka (1960), p. 11.

TABLE I. THE AGGLOMERATION TEMPERATURES OF VARIOUS KINDS OF METAL POWDERS IN A STREAM OF HYDROGEN OR IN AIR

Metal	Size, mesh	Fluidizing gas	Agglomeration temperature, °C	M. p., °C
Ag	−100+200	Air	85	960.8
Cu	−100+200	H_2	250	1083
Cu	−100+200	Air	>400	
Ni	−150+300	H_2	325	1455
Fe	−100+300	H_2	345	1535
Fe	−100+150	H_2	>420	
Stainless steel	−150+200	H_2	>390	

10% Nickel-Silica Catalyst.[3]—This catalyst was prepared by the super-coprecipitation method from a mixed-solution of nickel nitrate and sodium silicate, using ammonium carbonate at 20°C, and with vigorous stirring. The precipitate was washed with distilled water on the filter, dried at 100°C, and calcined at 550°C for 2 hr.

20% Nickel-Alumina and 20% Cobalt-Alumina.—The powdered alumina was added to a solution of cobalt nitrate. The slurry was stirred for some time, and to it these was then slowly added, at 20°C, a quantity of dissolved ammonium carbonate in a slight excess; the mixture was then heated and kept at 60—70°C for 5 hr. After it had been filtrated and washed, the precipitate was dried at 100°C and calcined at 500°C for 2 hr. The structure and properties of the catalysts were described in a previous report.[4]

The Fluidization Test.—An experimental method reported before[1] was used for the fluidization tests. The bed temperatures were measured with a thermocouple immersed in the bed. Fluidizing difficulties due to agglomerate formation were directly visible through the pyrex tube, but they could also be readily deduced from the pressure-drop readings.

Results and Discussion

(1) Metal powders showed agglomeration when heated in a stream of hydrogen. The experimental results are shown in Table I. The agglomeration temperature was influenced by many factors, such as the particle size and the kinds of gas used. In the case of silver, agglomeration was observed even in air at 85°C.

(2) The nickel-diatomaceous earth catalyst ceased to be fluidized after a few hours. The agglomerates which formed were of a relatively low mechanical strength. Cooling the bed to room temperature, while maintaining the gas flow, was sufficient to bring about fluidization again. If this cycle of heating and cooling was repeated several times, a gradual lowering of the agglomeration temperature, characterized by the cessation of fluidization, was observed, but after a still larger number of cycles this temperature appeared to tend toward a constant value (Table II, B).

TABLE II. INDUCTION PERIOD DATA OF THE AGGLOMERATION PROCESS OF Ni-DIATOMACEOUS EARTH

Catalyst	Run	Reaction temp., °C	Induction period, t, min.
(A)	1	350	20
New	2	350	30
Cat.	3	300	140
	4	325	30
	5	275	155
(B)	6	350	2
Repeated	7	325	6
catalyst	8	275	35
	9	275	24

When a fresh sample of nickel-diatomaceous earth powder was maintained at a constant temperature under the fluidizing conditions, difficulties due to agglomeration did not occur immediately. A time interval which depended on the bed temperature was observed. The "induction period" was, therefore, defined as the time interval between the beginning of fluidization and the first major decrease in pressure drop, a decrease which culminated in complete bed immobility. Such induction periods were not observed with the other catalyst compositions, but the possibility of their occurance after lengths of time greater than those used in our experiments (about 40 hr.) can not be ruled out. The induction-period data of the agglomeration process is given in Table II, A for the nickel-diatomaceous earth. The Arrehenius plot correlated the induction period as a function of the reciprocal bed temperature, so the data may be represented by an empirical equation:

$$\frac{1}{t} = A\exp\left(-\frac{\Delta E}{RT}\right) \quad (1)$$

Where t is the induction period (min.); T is the bed temperature, °K and A and E are experimental constants. E is regarded as the activation energy for the overall agglomeration process. The activation energy calculated from the slope of these line was about 22 kcal.

3) T. Shirasaki, R. Shioda, H. Hagiwara, G. Shin, M. Kato and K. Morikawa, *J. Chem. Soc. Japan Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **68**, 279 (1965).
4) H. Hagiwara and E. Echigoya, This Bulletin, **38**, 2163 (1965).

(3) At the reaction temperature, cobalt-alumina, nickel-alumina and nickel-silica catalyst powders could be fluidized satisfactorily for 40 hr. of continuous operation.

It was found from the above results that the nickel-diatomaceous earth catalyst in which the nickel is not combined with the carrier forms agglomerates under the reaction conditions, while the cobalt or nickel catalysts in which the metal forms a complex with the carrier resists the formation of agglomerates.

The cobalt-alumina catalyst found in this experiment was used for the experiments on the hydrogenation of aniline with a fluidized bed; good results were thus obtained.[5]

The agglomeration phenomena might be explained by connecting it with the sintering process of the metal.[6-8]

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5) E. Echigoya, H. Hagiwara and A. Sakurai, to be submitted.
6) W. D. Kingery and M. Berg, *J. App. Phys.*, **26**, 1205 (1955).
7) A. L. Pranatis and L. Seigle, *Powder Metallurgy*, **1**, 53 (1961).
8) G. C. Kuczinsky, *Acta Met.*, **4**, 58 (1956).