DISPERSITY OF CATALYST AND CATALYTIC ACTIVITY.

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A most simple case of mixed catalysts is that in which a mixture of two substances, the one catalytically active and the other inert, forms a catalyst. In hydrogenation catalysis, a catalyst composed of nickel with an irreducible oxide such as kieselguhr, alumina, magnesia, etc. may be cited as an example. The name promoters may be given to these oxides, when the addition of a small quantity of them greatly increases the catalytic activity of nickel. The oxides may be termed carriers or supports, when nickel is distributed on a large quantity of them, the activity being not materially enhanced. It is evident, however, that to class these oxides either as promoters or as carriers is not always possible, because no decisive line of demarcation can be drawn between them. The author has studied the hydrogenation of acetylene using the nickel-kieselguhr and palladium-kieselguhr catalysts. Attention has been devoted to the modification of the catalytic activity produced by admixture with inert substance. The quantity of kieselguhr added to the catalytic agent has considerable influence on the activity of the resulting catalyst. In the presence of nickel alone and with excess of hydrogen, acetylene is hydrogenated completely to ethane. By passage over nickel or palladium distributed on a suitable amount of kieselguhr, acetylene is hydrogenated exclusively to ethylene. The composition of the products depends on the relative proportion of nickel and kieselguhr or palladium and kieselguhr. These results suggest a possible mechanism of one case of promoter and carrier actions and on the other hand, a method of selective hydrogenation of acetylene to ethylene.

(1) A Possible Mechanism of One Case of Promoter and Carrier Actions. The phenomenon which is met with, namely the markedly selective action of catalysts produced by varying the dispersity of the catalytic agent on an inert substance, can not be explained from the standpoint of the problem of the quantity of a catalytic agent. This can hardly be due simply to the diminution in the amount of a catalyst, since the prolonged contact with a catalyst can not cause the production of ethane. In order to offer the explanation, the author assumes the co-activation of neighbouring active centres on the catalytic surface by the heat of reaction. A surface of catalyst may present centres of various degrees of activeness. At the start of a catalytic reaction, the centre of maximum activity, the point A, on the surface is activated and the reaction takes place at first on the point A. The reaction is exothermic and the heat of reaction may excite the neighbouring active point B and the reaction occurs on the point B. The heat of the reaction may excite not only the new active point C but also the original active point A, which is further stimulated. Thus the co-activation of active centres is achieved and the proportion of stimulated active points increased and the reaction correspondingly accerelated. After the attainment of equilibrium between accumulation and loss of heat, the reaction proceeds with constant velocity. Now the case may be considered in which a catalytically active substance is spread on a relatively large amount of non-catalytic material. If the dispersity of the catalytic agent is sufficiently large, the distance between the neighbouring active points on the surface may be long enough to disable the efficient co-activation, so that the catalytic centres can not display their full activities. There may be cases where the hydrogenation of acetylene to ethylene is possible but the hydrogenation to ethane is impossible. In most cases carriers are employed on purpose to increase the surface area of catalysts and to gain the superior activity. In this work the extreme case has been discussed in which the extent of distribution of catalytic metal on carriers is so great that the restriction of the activity can be observed. At the other extreme, the case in which a metal catalyst is admixed with a minute amount of inert oxides, may be considered. In such a case, the distance between the active points is nearly the same as that on the pure metal. The presence of an inert oxides, which is a bad conductor of heat, interspersed among the active centres, favours the accumulation of the reaction heat. The effect is the equivalent of an extremely high local temperature. Therefore, the co-activation of active centres being enhanced, the reaction velocity is greatly increased. The cases in which a metallic catalyst is stimulated by the presence of traces of irreducible oxides are very numerous and in the case where the reaction is a simple addition of hydrogen, the primary function of the promoter action may be regarded as the enhanced co-activation of active centres by the heat of reaction.

The author arrives at the conclusion with regard to the modification of a straight hydrogenation process—the simple addition of hydrogen at an unsaturated linkage—in presence of a metallic catalyst, an inert irreducible oxide such as kieselguhr, alumina, magnesia, etc. being employed as the promoter and as the carrier, that the stimulation and the restriction of catalytic activity can be satisfactorily explained on the basis of enhanced and unfavoured co-activation of active centres by the heat of reaction.

(2) **Hydrogenation of Acetylene to Ethylene.** In a series of investigations of von Wilde(1), Sabatier(2), and more recently Morris(3) it was shown that acetylene was easily hydrogenated to ethane, ethylene and liquid products in presence of metallic catalysts. Paal(4) and Ross(5) have investigated the hydrogenation to get ethylene and they were able to obtain the product containing 80% ethylene, the former employing colloidal palladium shaken with water, the latter in presence of nickel catalyst. Much attention has been given to the problem of preparing ethylene by the hydrogenation of acetylene, and several patents have been claimed for the technical hydrogenation. The author observed that acetylene was readily hydrogenated to ethylene by the employment of the palladium catalysts distributed on the proper amount of kieselguhr (500-1500 parts of kieselguhr added to one part of palladium). With equal volumes of acetylene and hydrogen the product contains 90% ethylene and 2-3% saturated hydrocarbons.

Experimental.

Acetylene was prepared by the action of water on calcium carbide. The removal of the impurities was accomplished by the method described in Vanino's "Präparativen Chemie." For the experiments with nickel catalysts, acetylene was solidified with liquid air and subjected to a fractional distillation. To poisons, nickel is more sensitive than palladium and without this treatment no satisfactory results were obtained. Hydrogen was obtained from cylinder of commercial electrolytic hydrogen and no attempt was made to remove the impurities except to bubble the gas through potassium hydroxide solution.

Nickel-kieselguhr catalyst was prepared by the reduction of nickel oxide admixed with kieselguhr, which was obtained by the calcination of the mixture of nickel nitrate and kieselguhr. Palladium-kieselguhr catalyst was prepared from palladium chloride solution, into which

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(1) von Wilde, *Ber.*, **7** (1874), 352.

(2) Sabatier et Senderens, *Compt. rend.*, **128** (1899), 1173; **130** (1900), 1559.

(3) Morris and Reyerson, *J. Phys. Chem.*, **31** (1927), 1332.

(4) Paal und Hoheneggen, *Ber.*, **48** (1915), 275.

(5) Ross, Culbertson and Parsons, *J. Ind. Eng. Chem.*, **13** (1921), 775.

kieselguhr was added, by reduction to metal with formaldehyde.⁽¹⁾ The solution was heated on water-bath until the precipitation of palladium was completed and then filtered. For palladium catalysts, commercial kieselguhr was used with no further purification and for nickel catalysts kieselguhr was purified by boiling with hydrochloric acid solution.

The experiments were carried out by the flow method. The apparatus used is represented in Fig. 1. A mixture of acetylene and hydrogen stored in the reservoir (1) was introduced through the manometer (2) and the flowmeter (3) into the catalyst tube (4) placed in a gas furnace. The tube was made of glass, 46 cm. long and 1.4 cm. in diameter. The temperature was indicated by the thermometer placed outside the tube. The reaction products were collected into the reservoir (5). The reservoirs (1) and (5) were three litre and one litre bottles respectively and saturated sodium chloride solution was used as a confining liquid. A U-glass tube, 1.5 cm. in diameter, was occasionally used as a catalyst tube for the experiments run at the temperatures below 130°C. The tube was filled with the catalyst supported on granules of quartz and immersed in a glycerin-bath. In carrying out the hydrogenation, the catalyst tube was heated to the desired temperature, hydrogen being streamed into the tube. And the mixture of acetylene and hydrogen in the reservoir (1) was passed over the catalyst. When about one litre of the gases was passed, it was felt that the system had reached a steady state. Then the product was collected into the reservoir (5) and the extend of hydrogenation was determined by the analysis of the product.

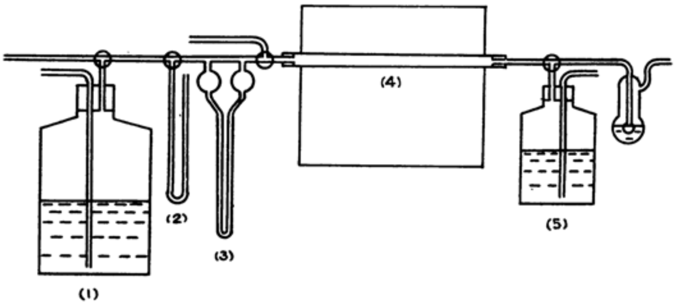

Fig. 1.

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(1) Willstätter und Waldschmidt-Leitz, *Ber.*, **54** (1921), 123.

Analyses of acetylene and ethylene were carried out according to the method of Treadwell(1) modified by Fujio(2). Acetylene, ethylene and heavy hydrocarbons were determined by the absorption with the solution of mercuric cyanide, mercuric nitrate and fuming sulphuric acid respectively. After the removal of the above gases, hydrogen and saturated hydrocarbons were estimated by oxidation with cupper oxide at 300°C. and 600°C. The saturated hydrocarbons consisted of ethane and methane.

(1) **Experiments on the Effects of Dispersity of Catalysts.** Mixtures of one volume of acetylene and nearly two volumes of hydrogen were passed over nickel-kieselguhr catalysts at the rate of flow 5 litres per hour. Mixtures of nearly equal volumes of acetylene and hydrogen were passed over palladium-kieselguhr catalysts at the rate of flow 7 litres per hour. The composition of the resulting gases greatly depends on the dispersity of catalysts on kieselguhr. In the presence of the catalysts of small dispersity, the hydrogenation proceeds to ethane and the production of ethylene decreases. Table 1 gives the results of the experiments.

Excess of hydrogen in the reacting gases favours the production of ethane and the tendency is remarkable in presence of the catalysts of small dispersity. Table 2 gives the results of the experiments.

(2) **Experiments on the Production of Ethylene.** The effects of variation in the composition of reacting gases, reaction temperature, the rate of flow, and the addition of steam to the gases in the hydrogenation, were observed in presence of palladium-kieselguhr catalysts. From the estimation of the volumes and the composition of the gases before and after the hydrogenation, the yields of the products were calculated. Tables 3 and 4 give the results. Table 5 gives the results of the experiments with palladium distributed on the purified kieselguhr and anhydrous silicic acid.

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(1) Treadwell und Tauber, *Helv. Chim. Acta*, **2** (1919), 601.

(2) Fujio and Shirai, *Kaigun Nenryôshô Jikkenhôkoku* (*Experimental Reports of the Japanese Naval Institute of Fuel.*), **4**, No. 4, 47.

Table 1.

Nickel-kieselguhr Catalysts

Parts of kieselguhr added to one part of nickel	Reaction temperature	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2*	CH_4	C_2H_6	N_2
0	100°	.0	.0	.9	34.8	57.9		6.4
20	100°	.0	5.1	1.1	43.9	41.5		8.4
100	100°	.0	15.8	.6	63.5	2.8	6.8	11.3
200	150°	.4	16.8	1.2	64.8	3.6	.8	12.2
500	200°	.9	12.6	1.1	70.8	2.8	.0	13.8

* Hydrogen was found in abundance, because acetylene underwent the polymerisation into liquid hydrocarbons.

Palladium-kieselguhr Catalysts

Parts of kieselguhr added to one part of palladium	Reaction temperature	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2
50	110°	3.8	67.3	.9	1.3	22.5	4.1
150	120°	2.7	79.5	.7	1.4	9.1	6.1
500	120°	1.2	91.3	.4	1.2	2.4	4.4
800	180°	2.2	88.4	.3	.2	1.7	7.1
1500	170°	2.3	90.2	.5	1.3	1.8	4.1

Palladium-kieselguhr Catalysts

Parts of kieselguhr added to one part of palladium	Reaction temperature	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2	
500	150°	1.8	90.7	.5	.0	2.6	4.4	Excess of acetylene
500	180°	2.2	91.4	.5	.0	1.1	4.8	Excess of acetylene
500	150°	1.0	83.2	.8	2.3	7.2	5.4	Excess of hydrogen
1500	200°	2.4	90.8	.2	.3	1.5	4.8	Excess of acetylene
1500	200°	1.3	84.7	.3	6.6	2.5	4.6	Excess of hydrogen
1500	150°	2.4	86.3	.8	3.1	2.6	4.8	Excess of hydrogen

Table 2.

Palladium-kieselguhr Catalysts (500 parts of kieselguhr added to one part of palladium)

Reaction tempera-ture	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydro-carbon	H_2	C_2H_6	N_2	Others*	
170°	6.0	Original	1600	47.8	—	—	49.4	—	2.7		
		Product	680	1.1	89.1	.3	.0	4.4	5.1		
		% of C_2H_2 converted to		1.0	79.3	—	—	3.9	—	15.8	
170°	6.0	Original	1800	50.5	—	—	47.3	—	2.2		
		Product	770	3.3	90.7	.4	.0	1.7	3.9		
		% of C_2H_2 converted to		2.8	76.8	—	—	1.4	—	19.0	
180°	6.5	Original	1700	39.2	—	—	57.8	—	3.0		Excess of hydrogen
		Product	810	2.3	50.1	1.2	27.1	11.5	5.6		
		% of C_2H_2 converted to		2.8	61.0	—	—	14.0	—	22.2	
170°	6.0	Original	1300	48.5	—	—	48.9	—	2.4		Addition of steam
		Product	570	2.4	90.4	.4	.0	1.6	5.4		
		% of C_2H_2 converted to		2.2	81.0	—	—	1.4	—	14.8	
185°	6.5	Original	1700	49.1	—	—	48.3	—	2.6		Addition of steam
		Product	710	.8	90.3	.4	1.9	2.7	4.9		
		% of C_2H_2 converted to		.7	76.7	—	—	2.3	—	20.3	
185°	6.0	Original	1700	49.6	—	—	48.3	—	2.1		
		Product	680	2.3	88.0	.5	1.6	2.1	5.4		
		% of C_2H_2 converted to		1.9	71.1	—	—	1.7	—	25.3	
180°	13.0	Original	1800	47.7	—	—	50.7	—	2.4		
		Product	750	2.7	80.5	.8	8.7	2.7	4.6		
		% of C_2H_2 converted to		2.4	70.3	—	—	2.4	—	24.9	
150°	7.0	Original	1600	38.5	—	—	59.2	—	2.3		Excess of hydrogen
		Product	630	2.7	53.3	.8	32.7	5.5	4.9		
		% of C_2H_2 converted to		3.6	70.1	—	—	7.2	—	19.1	
185°	6.0	Original	1700	50.1	—	—	47.9	—	2.0		Addition of steam
		Product	680	2.1	88.8	.7	1.7	1.7	5.0		
		% of C_2H_2 converted to		1.7	71.0	—	—	1.4	—	25.9	

Table 2.—(*Concluded*)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_2	Heavy hydrocarbons	H_2	C_2H_6	N_2	Others	
		Original	1800	48.0	—	—	49.9	—	2.1		U-glass tube used as catalyst tube
130°	7.2	Product	720	2.3	86.8	.4	.8	3.5	6.2		
		% of C_2H_2 converted to		1.9	72.3	—	—	2.9	—	22.9	
		Original	1800	49.7	—	—	47.6	—	2.7		U-glass tube used as catalyst tube
135°	12.3	Product	760	4.1	83.7	.6	5.5	1.6	4.4		
		% of C_2H_2 converted to		3.5	71·0	—	—	1.4	—	24.1	
		Original	1500	50.3	—	—	47.5	—	2.2		U-glass tube used as catalyst tube
100°	3.7	Product	600	4.6	81.5	1.0	4.7	3.2	4.9		
		% of C_2H_2 converted to		3.7	65.8	—	—	2.6	—	27.9	
		Original	1800	47.6	—	—	49.2	—	3.2		
110°	3.9	Product	760	3.3	81.1	1.2	.6	6.0	7.8		
		% of C_2H_2 converted to		2.9	71.8	—	—	5.3	—	20.0	

* Hydrogenation was accompanied by the polymerisation of acetylene to liquid hydrocarbons. The figures were determined by difference.

Table 3.

Palladium-kieselguhr Catalysts (1500 parts of kieselguhr added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2	Others	
		Original	1800	45.7	—	—	50.2	—	4.1		
190°	6.5	Product	800	2.9	78.3	.5	8.8	2.7	6.7		
		% of C_2H_2 converted to		2.8	76.1	—	—	2.6	—	18.5	
		Original	1400	37.5	—	—	60.4	—	2.1		Excess of hydrogen
200°	7.0	Product	780	1.4	49.1	.7	42.4	2.1	4.3		
		% of C_2H_2 converted to		2.1	73.0	—	—	3.1	—	21.8	

Table 3.—(*Concluded*)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbons	N_2	C_2H_6	H_2	Others	
200°	9.3	Original	1700	38.0	—	—	60.0	—	2.0		Excess of hydrogen
		Product	940	1.8	52.5	.8	38.2	2.2	4.5		
		% of C_2H_2 converted to		2.6	76.4	—	—	3.2	—	17.8	
200°	11.5	Original	1600	37.9	—	—	59.1	—	3.0		Excess of hydrogen
		Product	880	2.1	55.5	.8	32.0	3.9	5.7		
		% of C_2H_2 converted to		3.0	80.5	—	—	5.7	—	10.8	
200°	6.0	Original	1700	50.2	—	—	47.5	—	2.2		Addition of steam
		Product	700	2.2	86.9	.5	3.4	1.7	5.1		
		% of C_2H_2 converted to		1.8	71.2	—	—	1.4	—	25.6	
190°	5.5	Original	1700	49.0	—	—	47.9	—	2.1		Addition of steam
		Product	690	3.0	85.7	.9	4.3	1.6	4.5		
		% of C_2H_2 converted to		2.5	71.0	—	—	1.3	—	25.2	

Table 4.

Palladium-kieselguhr Catalysts (500 parts of purified kieselguhr added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2	Others
170°	7.0	Original	1800	49.3	—	—	48.8	—	1.9	
		Product	800	5.9	83.4	.7	3.6	2.7	4.6	
		% of C_2H_2 converted to		5.3	75.1	—	—	2.4	—	17.2
150°	5.0	Original	1700	49.0	—	—	48.0	—	2.0	
		Product	730	2.3	87.8	.7	1.3	3.7	5.3	
		% of C_2H_2 converted to		2.0	76.8	—	—	3.2	—	18.0
170°	6.2	Original	1700	37.1	—	—	59.9	—	3.0	
		Product	900	2.0	47.2	1.3	30.3	12.7	6.5	
		% of C_2H_2 converted to		2.9	67.3	—	—	18.1	—	21.7

Table 5.

Palladium-anhydrous silicic acid Catalysts (500 parts of anhydrous silicic acid added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C_2H_2	C_2H_4	Heavy hydrocarbons	H_2	C_2H_6	N_2	Others
150°	4.8	Original	1800	49.9	—	—	47.9	—	2.2	
		Product	740	4.0	88.1	.6	.0	4.2	3.1	
	% of C_2H_2 converted to			3.3	72.6	—	—	3.4	—	20.7
170°	9.0	Original	1800	49.2	—	—	48.7	—	2.1	
		Product	750	2.6	88.3	.8	.2	3.6	4.5	
	% of C_2H_2 converted to			2.2	74.8	—	—	3.1	—	19.9

Summary.

1. In the study of the hydrogenation of acetylene in presence of nickel and palladium catalysts distributed on kieselguhr, it was observed that markedly selective action of catalysts was produced by the variation of the dispersity of the catalytic agents on kieselguhr. The phenomenon which was met with, suggests a possible mechanism of one case of promoter and carrier actions and on the other hand, a method of hydrogenation of acetylene to ethylene.

2. With regard to the simple hydrogenation process, in presence of a metallic catalyst, inert irreducible oxides being employed as the promoter and as the carrier, stimulation and restriction of the catalytic activity can be explained on the basis of the assumed co-activation of active centres on the catalytic surface by the heat of reaction.

3. Acetylene was readily hydrogenated to ethylene by the employment of the palladium-kieselguhr catalysts of proper dispersity. With equal volumes of acetylene and hydrogen, the product containing more than 90 per cent. ethylene, was obtained.

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