[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WESLEYAN UNIVERSITY]

THE CATALYTIC PREPARATION OF UNSATURATED HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN[1]

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The work described in this article had its origin in an investigation of the catalytic synthesis of glycol, begun in this Laboratory in September, 1918, at the request of the Division of Chemistry and Chemical Technology of the National Research Council. During this investigation, it was found possible to obtain from carbon monoxide and hydrogen, organic liquids miscible as well as immiscible with water. Alcohols and aldehydes were present in the water-miscible product, and hydrocarbons in the oily material. Since liquid products were formed in largest amounts under pressure, and we were forced to dismantle the pressure apparatus available, later work was done at atmospheric pressure on the preparation of gaseous products, especially hydrocarbons. Although the catalytic preparation of several of the simpler hydrocarbons has been previously reported, we hope to contribute something to the determination of the conditions under which catalytic action seemed most favored, throw some light on the disagreement of Orlow[2] and Fester[3] regarding the production of ethylene from carbon monoxide and hydrogen, and finally make a preliminary survey of the field with the object of selecting problems for future investigation.

Hydrogen and carbon monoxide were obtained by passing steam over charcoal in a quartz tube, heated electrically with nickel-chromium or platinum resistance wire. If an increased proportion of carbon monoxide was desired, carbon dioxide was passed through the quartz tube with the steam. Additional hydrogen was obtained from tanks of the compressed gas. Streams of the different gases were passed through appropriate purification trains, regulating floating-bell gas holders, then through capillary flowmeters to control the proportions of the final mixture. At other times when less gas was being used, carbon monoxide was generated by running 90% formic acid into concd. sulfuric acid. If it was desired to remove all traces of oxygen, the components of the final gas mixtures were passed separately over heated copper. After collection in a larger gas holder, the mixed gases were thoroughly stirred by a fan driven from without through a gas-tight packing. Samples of the stored gases were removed and analyzed at frequent intervals.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 71st meeting of the American Chemical Society at Tulsa, Oklahoma, April 5–9, 1926.

[2] Orlow, *Ber.*, **42**, 893 (1909).

[3] Fester, *Brennstoff-Chem.*, **3**, 244 (1922). Fester and Brude, *Ber.*, **56**, 2245 (1923). Taylor, *J. Phys. Chem.*, **28**, 930 (1924).

Starting with air-heated, horizontal glass tubes as catalytic vessels, and simple, direct-connected condensers for removing reaction products, we found it desirable to change to metal containers; iron was first used, and later nickel. The cross-sectional area of the catalyst employed was decreased from 4 sq. cm. to slightly less than 1 sq. cm., and the temperature control made more exact by the use of oil, or preferably fusible metal baths. One form of the apparatus is shown in Fig. 1.

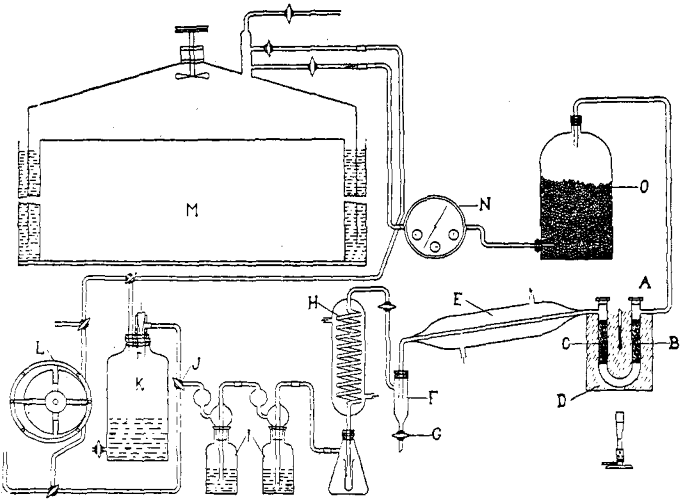

Fig. 1.

From a 1000-liter holder M, the mixed gases passed through a wet gas meter N, over dry lime in a 13-liter aspirator bottle O and into the nickel U-tube A containing the catalyst. Each arm of the U-tube contained compact layers, B and C, of catalyst, held in place by disks of nickel-chromium gauze. The effect of the walls of the nickel tube and the nickel-chromium gauze was considered to be negligible, as blank tests showed only traces of methane, the most probable product of catalytic action on nickel surfaces. Readily condensed liquids and samples of gases were withdrawn at G. Additional condensation surface, surrounded by special refrigerants, was offered in H. When desired, the exit gases could be passed through the wash bottles I, containing 1% solutions of sodium carbonate and potassium permanganate. Movement of the gas was produced by a water aspirator K or a mechanical pump L. By appropriate setting of stopcocks, gas could be discharged from the apparatus, returned to the holder or recirculated over the catalyst. The latter course was not used in obtaining the results given in this article, except to prevent waste of gas during preliminary reductions, and when catalysts were apparently inactive.

The rates of flow employed varied from 50 to 1000 cc. per minute through 20 cc. of 10–20 mesh catalyst, usually two layers in series, each 10 cm. deep and 1 sq. cm. in cross-sectional area. In the tables the gas velocity is stated as space velocity—that is, volume of gas over one volume of catalyst in one hour. The best yields of unsaturated hydrocarbons seemed to be obtained at space velocities of 1500 to 2000. In general the velocities employed in this investigation were higher than those previously reported.

The usual position of the dehydrating agent was next to the catalyst, as shown in Fig. 1, since for most catalysts the presence of water vapor in greater amounts than corresponding to 5 mm. pressure seemed to interfere with the production of hydrocarbons at low temperatures. On the other hand, a small amount of oxygen seemed to aid in the production of unsaturated hydrocarbons, and had the effect of lengthening the efficient life of the catalyst. About 1% of oxygen seemed to be the most desirable, but amounts up to 2% of oxygen and 8% of nitrogen interfered but slightly. Carbon dioxide apparently lessened the production of both saturated and unsaturated compounds. The effluent gas was frequently burned in an ordinary Tirrill burner or in a small glass and platinum burner. The luminosity of the flame gave some indication of the activity of the catalyst being tested.

The composition of the various mixtures of gases involved in this investigation was determined in general by the usual absorption methods with mercury as the confining liquid, where possible. The percentages given in the columns headed "unsaturated hydrocarbons" in Tables I–V were obtained in most cases from the contraction observed after treatment with fuming sulfuric acid and potassium hydroxide. However, at least six different methods of separating and determining unsaturated hydrocarbons were critically examined and used in one or more of the analyses recorded in Tables I–V. No indication of acetylene or benzene was observed, and consequently it seems reasonably certain that small amounts of ethylene or its homologs must have been present.

Small amounts of nickel carbonyl were produced in several experiments with nickel-palladium and nickel-platinum catalysts, when used at temperatures in the neighborhood of 100°. At temperatures above 175°, no indication of the presence of this compound was obtained. A simple sensitive test for volatile carbonyls is the formation of a bright white inner cone when gas containing carbonyl is burned in an ordinary Bunsen burner. If the carbonyl was not condensed by refrigerants or removed by the action of heat, it was decomposed by fuming sulfuric acid, liberating carbon monoxide. An increase of 1.5% was noted in one analysis. Since the carbonyl was not removed in several experiments in which unsaturated compounds were formed, it can be concluded that the recorded per cent. of unsaturated hydrocarbons may be slightly low in some cases. The

TABLE I

SINGLE-COMPONENT CATALYSTS

No.	Catalyst	Method of preparation	Support	Gas used		O_2, %	Space velocity	Temp., °C.	Unsatd. hydrocarbons, %	Satd. hydrocarbons, %	CO_2, %
				H_2, parts	CO, parts						
1	$CuCl_2$	Evapn. at 400°	Pumice	2	1	...	300	150–300	...	...	...
2	Pt	Decompn. of H_2PtCl_6	Asbestos	2	1	...	150–1050	150–300	...	...	3.0
3	UO_2	Decompn. of acetate, redcn. with H_2	Asbestos	2	1	...	300–1800	150–300	...	...	1.2
4	C	Active charcoal	....	2	1	...	300–1800	150–300	...	...	...
5	Al_2O_3	Dehydrn. of $Al(OH)_3$	....	2	1	...	300–1800	150–300	...	...	...
6	MnO_2	$KMnO_4 + H_2SO_4$	....	2	1	...	150–3600	150–300	...	...	3.2
7	Ni	Pptn. of $Ni(OH)_2$, dry, redcn. with H_2 at 300°	....	1	1	...	300	150	...	1.3	6.2
	Ni		....	1	1	...	300	200	...	1.9	30.0
	Ni		....	1	1	...	300	250	...	3.2	37.6
	Ni		....	1	1	...	300	300	...	7.9	40.0
8	Al	20-Mesh granular	....	1	1	...	300–900	100–300	...	...	...
9	Fe	Pptn. with $Fe(OH)_3$, dry, redcn. with H_2 at 300°	....	2	1	...	900	300	...	0.6	11.0
10	Ag	Redcn. of oxide with H_2 at 300°	Pumice	2	1	...	900	200	...	...	1.1
11	Cr	20-Mesh granular	....	2	1	...	150–1200	100–350	...	...	...
12	Cu	Decompn. of $Cu(NO_3)_2$, redcn. with H_2 at 400°	Pumice	1	1	0.8	1800	400	0.3	0.7	0.18
13	Co	Redcn. of $Co(OH)_3$ with H_2 at 400°	....	1	1	.8	450	400	...	1.67	6.5
	Co		....	1	1	.8	450	300	...	3.82	0.67
	Co		....	1	1	.8	450	200	0.87	1.97	.3
14	Fe	Pptn. of $Fe(OH)_3$, redcn. with H_2 at 400°	....	1	1	.8	1800	400	...	6.3	29.0
	Fe		....	1	1	.8	1800	300	...	5.3	12.6
15	Ni	Pptn. of $NiCO_3$, redcn. with H_2 at 300°	....	1	1	3.0	2400	300	...	2.68	2.2
	Ni	Pptn. of $NiCo_3$, redcn. with H_2 at 250°	....	2	1	...	2400	255	...	22.9	8.5
	Ni		....	2	1	...	3000	300	...	17.6	5.4

TABLE II

TWO-COMPONENT CATALYSTS

No.	Catalyst	Method of preparation	Support	Gas used CO, parts	Gas used H_2, parts	O_2, %	Space velocity	Temp., °C.	Unsatd. hydrocarbons, %	Satd. hydrocarbons, %	CO_2, %
16	Fe, MnO	Pptn. of (OH), redcn. with H_2 at 300°	....	2	1	...	600	300	...	...	16.2
17	C, Al	Mixed powders	....	2	1	...	300–1500	150–350	...	...	...
18	C, Pd	Pptn. of (OH) on active C, redcn. with 1 CO, 2 H_2 at 150°	Carbon	1	1	0.7	1500	95	0.34	1.2	1.0
19	C, Pd	Same as No. 18		1	1	.7	150	97	...	0.3	0.2
20	Ni, Pd	Pptn. of (CO_3), redcn. with CO + H_2 at 250°	Carbon	1	1	.7	1350	93	.54	2.0	.68
	Ni, Pd			2	1	.7	1350	350	...	25.8	30.6
21	Ni, Pd	Decompn. of (NO_3), redcn. with H_2 at 250°	Pumice	1	1	...	1500	100	...	0.8	0.4
22	Ni, Pd	Decompn. of (NO_3), redcn. with H_2 at 500°	Porcelain	1	1	...	1500	335	...	2.78	2.13
23	Ni, Pd	Pptn. of (CO_3), redcn. with H_2 at 250°	Pumice	1	1	.83	900	103	1.48	3.38	1.85
	Ni, Pd			1	1	.83	1050	210	0.2	0.5	0.61
	Ni, Pd			1	1	.83	1050	300	...	1.74	1.6
24	Ni, Pd	Pptn. of (CO_3), dry separately, mix granules, redcn. with H_2 at 200°	Infusorial earth	1	1	1.9	3000	170	.1	8.8	21.9
25	Ni, Pd	Pptn. of (CO_3), mix, dry, redcn. with H_2, 200°		1	1	1.9	1200	202	...	2.6	1.77
	Ni, Pd			1	1	1.9	1200	107	.25	0.6	0.85
	Ni, Pd			1	1	1.9	1200	95	.44	.4	.5
	Ni, Pd			1	1	1.9	1200	85	...	...	.3
26	Ni, Pd	Pptn. together as (CO_3), redcn. with H_2 at 130°		1	1	1.9	1800	100	.35	.85	.25
27	Ni, Pd	Pptn. together as (CO_3), redcn. with H_2 at 160°		1	1	1.9	900	124	.45	9.68	24.3
28	Ni, Pd	Same as No. 27		1	1	1.9	1800	128	...	1.75	0.7
				satd. with H_2O							
29	Ni, Pd	Same as No. 27		1	1	1.9	1800	98	.2	...	.35
30	Ni, Pd	Pptn. together as (CO_3), redcn. with H_2 + CO at 200°		1	1	1.9	1800	101	1.57	2.02	3.6
31	Ni, Pd	Same as No. 30	Pumice	1	1	1.8	1800	103	2.1	3.8	4.7

TABLE II (*Concluded*)

No.	Catalyst	Method of preparation	Support	Gas used					Unsatd. hydrocarbons,	Satd. hydrocarbons,	
				CO, parts	H_2, parts	O_2, %	Space velocity	Temp., °C.	%	%	CO_2, %
32	Ni, Pd	Pptn. together as (CO_3), addn. of gran. Al, redcn. with $H_2 + CO$ at 250°	Gran. Al	1	1	1.8	1200	93	2.3	9.1	18.7
33	Ni, Pd	Decompn. of (NO_3) on gran. Al at 400°	Gran. Al	1	1	1.1	750	105	1.0	1.2	1.4
	Ni, Pd			1	1	1.1	2550	100	1.2	0.9	1.9
34	Ni, Pd		Gran. Al	2	1	0.9	750	103	0.5	2.3	3.1
35	Ni, Pd	Same as No. 23, but after 30 hrs.' run	Pumice	1	1	.8	900	101	.68	2.9	3.7
36	Ni, Pd	Pptn. of (CO_3), redcn. with $H_2 + CO$ at 200°	Pumice	1	2	.8	1500	102	2.2	1.1	6.8
37	Ni, Pd	Same as No. 36		2	1	.8	1500	99	0.96	2.4	3.5
38	Ni, Cu	Pptn. of (OH), dry, redcn. with $H_2 + CO$ at 290°	Pumice	1	1	1.2	1800	248	.3	3.1	1.5
	Ni, Cu		....	1	1	1.2	1950	127	...	...	3.3
39	Ni, Co	Decompn. of (NO_3), redcn. with H_2 at 250°	Inf. earth	1	1	1.2	1200	160	...	0.4	2.8
	Ni, Co			1	1	1.2	1500	139	...	3.1	15.4
40	Co-Cu-Cl_2	Dehydrn. of (Cl)	Pumice	2	1	...	300	150–300	...	...	...
41	Co, Cu	Pptn. of (OH) dry, redcn. with H_2 at 200°	....	1	1	0.9	600	200	...	2.7	10.2
	Co, Cu		....	2	1	.6	1050	200	.2	6.1	13.2
42	Co, Fe	Pptn. of (OH), dry, redcn. with $H_2 + CO$ at 300°	....	2	1	...	1500	300	...	5.3	8.7
43	Ni, Ag	Pptn. of (OH), dry, redcn. with H_2 at 200°	Pumice	2	1	...	1200	150	...	0.5	8.4
44	Cu, Pd	Pptn. of (CO_3), dry, redcn. with H_2 at 200°	....	1	1	...	1500	108	.1	1.6	3.8
	Cu, Pd		....	1	1	...	1500	160	...	9.4	11.3
45	Cu, Pd	Pptn. of (CO_3), dry, redcn. with $CO + H_2$ at 200°	....	1	2	...	1650	110	.4	0.7	1.1
46	Cu, Co	Pptn. of (OH), dry, redcn. with H_2 at 200°	....	1	2	...	1200	205	...	.8	0.9
47	Ni, Pd	Same as No. 45	Pumice	1	1	.6	1350	106	1.2	3.2	4.1
	Ni, Pd			1	1	...	1200	102	0.51	2.9	4.4
48	Ni, Pt	Pptn. of (OH), addn. of gran. Al, dry, redcn. at 450°	Gran. Al	1	1	1.1	1125	200	1.1	9.8	16.85

TABLE III

THREE- AND FOUR-COMPONENT CATALYSTS

No.	Catalyst	Method of preparation	Support	Gas used		O_2, %	Space velocity	Temp., °C.	Unsatd. hydrocarbons, %	Satd. hydrocarbons, %	CO_2, %
				H_2, parts	CO, parts						
49	Cu, Ni, Fe	Pptn. of (OH), dry, redcn. with H_2 at 300°	....	2	1	0.5	300	250	...	6.6	8.2
50	Cu, Co, Fe		....	2	1	.65	300	300	...	1.7	30.8
	Cu, Co, Fe		....	2	1	.65	300	200	0.3	7.6	13.6
	Cu, Co, Fe		....	2	1	.65	300	150	...	0.5	1.6
	Cu, Co, Fe		....	2	1	.65	1500	220	.47	5.1	11.3
51	Cu, Co, Ag	Pptn. of (OH), dry, redcn. with H_2 + CO at 200°	....	1	1	.8	750	325	....	...	17.6
52	Cu, Co, Ni	Pptn. of (CO_3), dry, redcn. with H_2 at 250°	....	2	1	.4	1800	170	.33	8.9	9.4
53	Cu, Co, Ni	Same as No. 52	Pumice	2	1	.5	1710	250	.17	3.2	7.4
54	Ni, Co, Pd	Pptn. of (CO_3), dry, redcn. with H_2 at 170°	....	2	1	1.8	2100	138	.16	0.1	0.45
	Ni, Co, Pd		...	2	1	1.8	2100	100	...	...	.25
				Moist							
55	Ni, Cu, Pd	Pptn. of (CO_3), dry, redcn. with CO + H_2 at 250°	....	2	1	0.55	1500	108	.48	1.3	.42
55	Ni, Cu, Pd	Same as No. 55	....	1	1	.74	1800	100	1.41	3.4	4.5
57	Ni, Cu, Pd	Pptn. of (CO_3), addn. of gran. Al, dry, redcn. with CO + H_2 at 200°	Gran. Al	1	1	.76	1650	107	2.9	9.1	14.8
58	Ni, Cu, Pd	Same as No. 57	Gran. Al	1	1	.8	2100	99	1.7	5.6	8.6
59	Fe, Ni, Pd	Pptn. of (CO_3), addn. of gran. Al, dry, redcn. with CO + H_2 at 200°	Gran. Al	1	1	.85	1950	135	2.4	11.4	15.7
60	Cu, Co, Fe, MnO	Pptn. of (OH), redcn. with H_2 at 300°	....	2	1	.74	600	300	...	1.4	22.0
61	Fe, Ni, Cu, Pd	Pptn. of $(CO_3,)$ redcn. with H_2 + CO at 200°	....	1	1	.92	1800	125	0.7	8.3	5.4
62	Fe, Ni, Cu, Pd	Same as No. 61	....	1	1	.92	1200	130	...	5.7	3.8

percentages of saturated hydrocarbons recorded in the tables were obtained from combustion data, and in general indicate amounts of methane. In a few analyses, especially those of gases obtained with catalysts containing copper, a small amount of ethane was found.

Typical data obtained from the experiments conducted are given in Tables I–V.

Copper and cobalt were the only single substances showing any evidence of production of unsaturated compounds, the amount obtained with copper being so small as to make its activity uncertain, and the efficient life of the cobalt catalyst was very short.

In general the two-component catalysts, possibly activated by small amounts of compounds of aluminum and sodium or potassium, showed the greatest activity. Palladium apparently promotes the formation of unsaturated compounds by nickel. Platinum seems to fulfil the same function, but less satisfactorily. With the exception of cobalt and possibly copper, an interface of two metals is apparently essential to the formation of unsaturated compounds. Other effects are summarized in Tables IV and V.

TABLE IV

EFFECT OF COMPOSITION OF GASES

	Ni-Pd unsatd., %	Cu-Co unsatd., %
1 CO:2 H_2	0.97	0.2
1 CO:1 H_2	2.1	.0
2 CO:1 H_2	2.2	.0

INTIMACY OF MIXING NI PD

	Unsatd. hydrocarbons, %
Mixture of 20-mesh granules	0.1
Mixture of suspension of ppts.	.44
Precipitated together	.35

TABLE V

COMPARISON OF METHODS OF PREPARATION OF NICKEL-PALLADIUM CATALYSTS

Reduction temperatures 250° to 300°

Runs at 95° to 105°

	Unsatd. hydrocarbons, %	Satd. hydrocarbons, %	Time to decrease efficiency 50% for unsatd. compds., hrs.
Ppt. with Na_2CO_3, wash, coat with granular pumice, dry, reduce with mixture of H_2 + CO at 200°..	2.1	3.08	10
Ppt. with Na_2CO_3 on infusorial earth, wash, dry, reduce with H_2 at 250°......................	0.45	9.7	20
Same as preceding but reduce with mixture of H_2 + CO..	1.57	2.02	20
Same as preceding but on pumice stone..........	1.48	3.4	30
Ppt. with Na_2CO_3 on granular aluminum, wash, dry, reduce with H_2 + CO at 250°............	3.2	7.9	30

In explanation of Table V and the last part of Table IV, it may be stated that the usual method of preparing catalysts for this investigation was by precipitating the oxide, hydroxide or carbonate in conveniently large volumes, taking into consideration subsequent washing; washing by decantation; filtering so as to form a solid cake; drying slowly over long periods of time in an electric oven; crushing and sieving to 20–40-mesh granules; finally, reducing with pure, dry hydrogen or hydrogen and carbon monoxide at temperatures from 160–300°. As indicated in the last part of Table IV, more intimate mixing favors the production of unsaturated hydrocarbons. Mixed catalysts usually contain equal weights of each substance indicated except palladium and platinum, of which metals one-tenth of the weight of other metals was used.

It was found that the same weight of catalyst was more effective if placed upon granules of inert material. For this purpose, infusorial earth and carbon did not behave as satisfactorily as pumice stone and aluminum. Granular aluminum was originally added to increase the heat conductivity, for while a thermocouple imbedded in the catalyst showed only small differences in temperature between heating-bath and catalyst, it was thought the close temperature control found necessary would be facilitated by such material. However, the pronounced effect produced can hardly be attributed to the better temperature control; it seems more probable that a small amount of alumina was formed during the preparation as outlined above, and this activates the mixture of metals. Another factor which may have played some part in the change produced was the presence of a trace of sodium carbonate or hydroxide and possibly nitrate in the catalyst, due to the difficulty of washing the gelatinous precipitates obtained in the first step of the process outlined above. Catalysts precipitated with sodium or potassium carbonates seemed to be the most active.

While the amounts of unsaturated compounds obtained were small—saturated compounds were not especially studied—and the variable experimental conditions were so large in number that positive conclusions are difficult to deduce, it is interesting to speculate on one or two questions. The short life of the catalyst producing unsaturated compounds may be due to the destruction of a metal-oxide interface by the complete reduction to metal or the complete masking of metal surface with deposited carbon. Such metal-oxide interface seems to be essential to the production of unsaturated compounds. In support of this idea it was found that many catalysts after becoming inactive contained free carbon; oxygen lengthened the life; longer life was accompanied by large production of carbon dioxide; high temperature or prolonged reduction reduced the activity of the catalyst; activity was partly restored by reoxidation and reduction.

Assuming that a metal-oxide interface is necessary, ethylene may be formed on the oxide, or oxide and activator surface, by the dehydration of methyl alcohol or formaldehyde, which are possible intermediate compounds in the more favored reaction of producing methane. The hydrogenation of the ethylene is prevented by the poisoning effect of carbon monoxide on the metal surface adjoining.

From these results we conclude that small amounts of ethylene can be formed by the catalytic reduction of carbon monoxide under special conditions. Owing to the small amounts produced, the short life of the catalyst, and the difficulty of securing consistent results, the commercial production of this substance does not seem feasible at atmospheric pressure.

Summary

A mixture of approximately equal parts of carbon monoxide and hydrogen with a trace of oxygen, when passed at a space velocity of from 1500 to 2000 over a nickel-palladium catalyst supported on aluminum or pumice stone, produced from 1 to 3% of ethylene at temperatures in the neighborhood of 100°. The catalyst lost one-half of its efficiency in 30 hours.

Other catalysts in order of decreasing activity were nickel-copper-palladium, iron-nickel-palladium, nickel-platinum, copper-cobalt-iron, copper-palladium, copper-cobalt-nickel, carbon-palladium, nickel-copper, copper-cobalt.

While saturated hydrocarbons were not especially sought, nickel and nickel-palladium catalysts yielded from 20 to 25% of methane at temperatures in the neighborhood of 250°. The catalysts showed little decrease in activity after several days' use.

MIDDLETOWN, CONNECTICUT

[CONTRIBUTION FROM THE SECTION ON PHYSICS OF THE MAYO CLINIC AND THE DIVISION OF EXPERIMENTAL SURGERY AND PATHOLOGY OF THE MAYO FOUNDATION]

THE CATALYTIC AND SPECIFIC DYNAMIC ACTIONS OF CERTAIN AMINO ACIDS[1]

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Introduction

The lack of any generally accepted explanation for the differences in the actions of the various amino acids in promoting oxidation in the animal organism suggested further investigation of the effects of these compounds on oxidation *in vitro*. Using the method of oxidation potentials developed by Clark[2] and his associates, we have studied the action of hydrogen

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[1] Read before the American Chemical Society, Philadelphia, Pennsylvania, September 6–11, 1926.

[2] Clark, Cohen, Sullivan and Gibbs, *U. S. Pub. Health Repts.*, **38**, 443, 666, 933, 1669 (1923); **39**, 381, 804 (1924); **40**, 649, 1131 (1925); *U. S. Pub. Health Repts., Suppl.*, No. 54, 55.