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THE SPECIFICITY OF DIFFICULTLY REDUCIBLE OXIDE CATALYSTS FOR HYDROGENATION

By J. V. VAUGHEN AND WILBUR A. LAZIER

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As a result of Sabatier's classical researches it has been known for over twenty years that certain metallic oxides catalyze the dehydrogenation of alcohols.¹ Although the capacity of these same oxides for catalyzing hydrogenation reactions may have been suspected at an early date, no use apparently was made of the fact until the discovery and commercial development of methanol synthesis. Sabatier and Fernandez² have since succeeded in hydrogenating nitrobenzene, alkyl nitrites and nitriles in the vapor phase using zinc and manganese oxides as catalysts.

In the dehydrogenation of ethanol and alcohols of higher molecular weight the major reaction is always accompanied by a certain amount of dehydration, resulting in the formation of alkenes as by-products. If dehydrogenating oxides are, like the metals, also hydrogenation catalysts of general applicability, the by-product alkenes should be hydrogenated to alkanes under the conditions of the reaction. As a matter of fact these compounds are not formed in appreciable amounts when zinc oxide is the catalyst.³

The above considerations led us to suspect that the hydrogenating oxides are specific in their action, but no comprehensive test of the point in question appears to have been made. The present paper is therefore concerned with the results obtained in the application of certain oxide catalysts to the hydrogenation of two representative systems of unsaturated compounds.

Results

The simple alkenes and acetone were selected as suitable materials for the hydrogenation tests. They are relatively stable and have been readily hydrogenated before by the use of reduced metals. Previous work assured the selection of conditions likely to avoid all predictable causes of failure excepting lack of catalytic activity.

Hydrogenation of Simple Alkenes.—Mixtures of ethylene, propylene, and butylene with hydrogen were passed repeatedly over the oxides of zinc, manganese, magnesium, molybdenum, vanadium and titanium, prepared in an active condition, at temperatures ordinarily suitable for other reactions catalyzed by these same oxides. In addition, representa-

¹ Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 252.

² Sabatier and Fernandez, *Compt. rend.*, **185**, 241 (1927).

³ Adkins and Lazier, *THIS JOURNAL*, **46**, 2297 (1924).

tive oxides were combined with other oxides known to serve as promoters for the hydrogenating-dehydrogenating oxides in other reactions. Control tests were made by employing a few metal catalysts.

The course of the reaction was followed by noting the change in volume and composition of the gas mixture. The results of these experiments are presented in Table I, where it is shown that in no case did a pure oxide or oxide mixture give a change in volume greater than could be accounted for as experimental error. In analyzing the exit gases, the increase in the percentage of saturated hydrocarbons resulting from passage over the catalyst was negligible, demonstrating that hydrogenation takes place very slowly, if at all.

On the other hand, reduced copper and a catalyst prepared by depositing metallic zinc on zinc oxide hydrogenated the gas mixture rapidly under the conditions used for the oxides. The results of these experiments proved that the equilibrium was entirely favorable.

TABLE I
HYDROGENATION OF SIMPLE ALKENES

Catalyst composition	Alkene	Temp., °C.	Comp. of entrance gas, %		% Vol. change	Alkene in exit gas, %	Conversion, %	
			Hydrogen	Alkene				
ZnO (<i>Ex</i> -hydroxide)	C ₂ H ₄	400	51.0	49.0	...	- 0.4	...	Negligible
ZnO (<i>Ex</i> -oxalate)	C ₂ H ₄	400	58.7	41.3	...	0.0	< 5.7 ^a	Negligible
ZnO (<i>Ex</i> -oxalate)	C ₂ H ₄	500	60.2	39.2	...	+ 0.9	< 4.7	Negligible
Mo ₂ O ₃	C ₂ H ₄	400	58.7	36.5	0.2	- 0.8	0.6 ^b	Negligible
V ₂ O ₃	C ₂ H ₄	400	48.5	48.7	< 2.8	+ 0.3	< 1.7 ^c	Negligible
MnO (<i>Ex</i> -hydroxide)	C ₂ H ₄	400	51.0	49.0	...	- 1.6	...	Negligible
MnO (<i>Ex</i> -oxalate)	C ₂ H ₄	400	60.5	39.5	...	0.0	0.2	Negligible
MgO	C ₂ H ₄	400	62.5	37.5	...	+ 1.3	< 1.0	Negligible
TiO ₂	C ₂ H ₄	400	53.4	44.3	< 2.0	0.0	< 2.3	Negligible
ZnO-Cr ₂ O ₃	C ₂ H ₄	400	51.0	49.0	0.0	0.0	...	Negligible
ZnO-Al ₂ O ₃	C ₂ H ₄	400	61.3	36.5	2.2	+ 0.7	2.6	Negligible
ZnO + 1.0% Fe	C ₂ H ₄	400	49.4	46.1	< 3.7	0.0	...	Negligible
ZnO + 0.2% Cd	C ₂ H ₄	400	51.0	49.0	0.0	- 2.6	...	Trace
Zn on ZnO (distilled)	C ₂ H ₄	400	51.6	43.2	0.5	-27.0	35.0	53
Zn on ZnO (reduced)	C ₂ H ₄	400	80.0	20.0	8.1	30
Reduced copper	C ₂ H ₄	221	54.0	46.0	...	-45.3	...	98
ZnO	C ₃ H ₆	400	64.6	35.4	0.0	- 1.3 ^d	...	Negligible
Mo ₂ O ₃	C ₃ H ₆	400	66.8	33.2	0.0	- 7.6 ^d	1.2	Negligible
ZnO	C ₃ H ₆	400	66.7	33.3	< 3.4	0.0	< 2.5	Negligible
Mo ₂ O ₃	C ₃ H ₆	400	67.6	30.4	< 1.9	- 0.7	< 1.2	Negligible

^a Values preceded by the < sign contain the nitrogen content as well as alkane.

^b A slight increase in saturated hydrocarbon may indicate polymerization of the alkene.

^c CO and CO₂ were formed even though the catalyst was reduced for three and one-half hours at 400° previous to the experiment.

^d Considerable carbonization on the catalyst.

An interesting result was obtained by reducing zinc oxide with very dry hydrogen at 500° and employing the resulting catalyst for the hydro-

generation of a dry, oxygen-free gas mixture. During reduction, the zinc oxide developed a gray color and hydrogenation took place where none had been observed with the unreduced oxide and moist gas. Other tests were made on samples of zinc oxide containing 1% of iron and 0.2% of cadmium, both reduced with hydrogen at 400°, in order to determine whether the hydrogenation reaction could be used as a method for detecting small amounts of easily reducible oxides in larger quantities of the difficultly reducible oxides. The negative results obtained indicate that the method is not sensitive to the concentrations tried, perhaps for the reason that zinc oxide inhibits the rapid reduction of small quantities of iron or cadmium oxides.

Hydrogenation of Acetone.—Difficulties are at once confronted in attempting the hydrogenation of compounds containing unsaturated carbon-oxygen linkages. Metallic oxides require high temperatures for activation, and at these temperatures the equilibria in the various reaction systems are apt to be quite unfavorable to hydrogenation at ordinary pressure. This is true in particular for compounds containing the carbonyl group. Rideal⁴ has given experimental values for the equilibrium constant in the system acetone-isopropanol-hydrogen up to 275°. By extrapolation of these data it may be shown that the theoretical conversion of a mixture of 1% acetone vapor in hydrogen at atmospheric pressure is only about 1% at 350°, the lowest temperature at which a measurable activity may be expected for zinc oxide.

As this value seemed to offer some promise of permitting a test for catalytic activity, several experiments were carried out at atmospheric pressure using a reduced copper and a zinc oxide catalyst. With the copper catalyst considerable acetone was recovered unchanged, but the condensate also contained isopropanol as determined by distillation. The gaseous reaction products contained a large percentage of *saturated* hydrocarbon. With zinc oxide, practically all of the acetone reacted to form a hydrocarbon gas together with a trace of unidentified oily products, but in this case the hydrocarbon was *unsaturated*.

The expected importance of the application of pressure in overcoming the unfavorable equilibrium was amply verified by other experiments which were carried out at 370° and an average pressure of about 150 atmospheres. Under these conditions, acetone was passed over zinc oxide catalysts with five times the quantity of hydrogen theoretically required for complete hydrogenation.

With a zinc oxide-chromium oxide catalyst of the type developed for methanol synthesis, the condensate contained isopropanol equivalent to a 16% conversion. A large part of the acetone was recovered unchanged, but there was also a small amount of oily material containing acetone

⁴ Rideal, *Proc. Roy. Soc. (London)*, **A99**, 153 (1921).

condensation products which were not satisfactorily identified. The effluent gas contained 5.5% of propylene but no propane. This gas presumably was formed by dehydration of isopropyl alcohol and represented a considerable loss of acetone. In order to eliminate this difficulty, the use of a dehydration repressor previously described in the patent literature⁵ was resorted to. It is stated therein that alkalis show a tendency to repress dehydration of alcohols undergoing dehydrogenation and dehydration by oxide catalysts having a mixed action. Consequently a second run was made in which the zinc oxide-chromium oxide catalyst was impregnated with about 5% of sodium carbonate. Under the same conditions as before, a conversion of acetone to isopropanol of 13.3% was obtained, and no propylene could be detected in the exit gas.

The above results not only prove conclusively the applicability of oxides to the hydrogenation of carbonyl compounds, but confirm the reported action of alkalis in repressing dehydration of alcohols.

Discussion

In investigating the reactions of alcohols over titania, Engelder⁶ noted the formation of saturated hydrocarbons. Although he was unable to obtain hydrogenation of alkenes over his catalyst, he believed that ethylene in the "nascent" state might be so hydrogenated. Bischoff and Adkins⁷ thought the reaction to be an auto-oxidation and reduction of the alcohol resulting in the formation of aldehyde as the other product. Our results on the hydrogenation of ethylene confirm Engelder's observations that titania is not a catalyst for this reaction. The results on acetone hydrogenation, however, are not in harmony with the idea that nascent alkenes may be hydrogenated where ordinary alkenes may not. In hydrogenating acetone over zinc oxide, propylene was obtained which must have been in the so-called nascent state at the moment of its formation, but no hydrogenation to propane took place.

In a comprehensive paper on hydrogenation with metal catalysts Schmidt⁸ has given the impression that hydrogenation with oxides is best explained by assuming the presence of a layer of reduced metal on the oxide surface. It seems rather improbable that reduced metal was present in the surface of any of the pure oxides employed in alkene hydrogenation, even though they were exposed to a reducing atmosphere at high temperatures. All have very high heats of formation, that of zinc oxide being the lowest. G. B. Taylor and Starkweather⁹ have presented data showing that a water vapor pressure of 0.0033 mm. will prevent reduc-

⁵ E. I. du Pont de Nemours and Co., French Patent 657,505, July 13, 1928.

⁶ Engelder, *J. Phys. Chem.*, **21**, 679 (1917).

⁷ Bischoff and Adkins, *THIS JOURNAL*, **47**, 817 (1925).

⁸ Schmidt, *Z. physik. Chem.*, **118**, 193 (1925).

⁹ Taylor and Starkweather, *THIS JOURNAL*, **52**, 2323 (1930).

tion of this oxide at 419°. Inasmuch as our gas was stored over water at 20° it contained more than sufficient water vapor to compensate for any possible error in this value and an ample amount to prevent reduction. It was only with some difficulty that we were able to prepare by reduction a concentration of zinc on zinc oxide sufficient for detection by hydrogenation of ethylene, and in this case a portion of the zinc formed was deposited as a film on the tube wall at a point beyond the hot zone of the furnace. This is not surprising in view of the fact that the vapor pressure of zinc at its melting point is 0.11 mm.,¹⁰ and any zinc metal remaining on the oxide surface must have been held there by adsorption.

It is believed that sufficient evidence has been adduced to show that certain difficultly reducible oxides are incapable of catalyzing the hydrogenation of the alkene linkage at an appreciable rate under the usual conditions of thermal activation, while they are at the same time capable of hydrogenating organic groups containing unsaturated oxygen atoms. In this respect they differ markedly from the reduced metals, which are capable of catalyzing the hydrogenation of both types of compounds with facility. Any theory elucidating the mechanism of catalytic hydrogenation must explain this difference in behavior. If the difference between oxides and metals is assumed to be one of degree rather than of kind, then the reason for the difference in the rates of reaction for different types of reactions becomes equally difficult to explain.

Various acidic oxides such as chromium oxide and alumina have found extensive use in methanol synthesis as promoters for the more basic hydrogenating oxides. Whatever the benefit for the reaction in question, the device seems inadequate to activate oxides for hydrogenation of the alkene linkage. Neither chromium oxide nor alumina produced any effect on the activity of zinc oxide toward alkene hydrogenation.

In attempting to explain the dual action of oxides in dehydration and dehydrogenation of alcohols and the action of repressive agents, H. S. Taylor¹¹ has suggested that processes of dehydrogenation and hydrogenation are attributable to metal ions and those of hydration and dehydration to oxide ions. So simple an explanation does not appear to be wholly adequate in the light of our results, since zinc oxide contains zinc atoms as does metallic zinc, yet the elemental metal hydrogenates alkenes rapidly while the oxide is quite inert.

The specificity of oxides as hydrogenation catalysts seems to indicate that there is an especial affinity of the oxide surface for compounds containing oxygen atoms which is not displayed for the alkenes. According to a modern variant of the adsorption theory of catalysis, the kind of ad-

¹⁰ Egerton, *Phil. Mag.*, **33**, 33 (1917).

¹¹ Taylor, "Colloid Symposium Monograph." **4**, 25 (1926); *Z. Elektrochem.*, **35**, 543 (1929).

sorption important in catalysis is thought of as being chemical in nature and resulting in the formation of a loosely constructed compound (possibly through a sharing of electrons) between the organic compound to be hydrogenated and the surface of the catalyst. In the case of the oxides it seems reasonable, as Taylor has suggested, to assume that the metal ion is the only component of the crystal lattice possessing sufficient affinity for the negative unsaturated group of the organic compound to cause the type of union necessary for activation. This view is held also by Schmidt.¹² In the case of carbonyl compounds, the "adsorption bond," is assumed to be established between zinc and oxygen, and a bond of much less strength is probably formed between zinc and an alkene linkage. But this alone does not explain the difference between zinc metal and zinc oxide.

Since hydrogen enters into all of the reactions concerned, the mechanism of its activation is apparently not a deciding factor. We have, however, been led to an explanation which is presented here in bare outline. The view is now widely held that the affinity or free valence of a metal atom manifested by catalytic activity is dependent on the degree of isolation of the active atom. It is suggested here that it is also dependent on the nature of the surrounding atoms in the crystal lattice. The more negative the surrounding atoms in the crystal, the more completely saturated are the metal atoms at the surface or in the other exposed or isolated positions. Hence, in zinc oxide the zinc atoms may be strongly held by oxygen, resulting in relatively feeble residual surface forces. In other words, the valence electrons may be distorted from their normal positions toward the inside of the crystal lattice. In zinc metal, however, there is probably less affinity of zinc atoms for other zinc atoms, resulting in a surface which is consequently quite highly unsaturated, indeed so much so that even the feebly attracted ethylene group is activated. In zinc oxide the surface valence of the metal atom may be dissipated to such an extent that the more weakly negative groups are no longer able to form a union with the surface of adequate stability or of the proper configuration to permit reaction with activated hydrogen. With such a surface a favorable adsorption complex results only with compounds like nitrobenzene, acetone, nitriles, etc.

The hypothesis is capable of considerable extension, for it is possible to visualize for any hydrogenating metal the existence of a series of lattice catalysts of graded intensity, consisting of the simple compounds of the metals with the non-metals. A similar series is predictable for compounds containing typical unsaturated groups.

Experimental Details

Apparatus and Method.—Owing to the wide diversity of experimental conditions employed in this work, three completely different types of ap-

¹² Schmidt, *Z. physik. Chem.*, **118**, 193 (1925).

paratus were used. While two of these were employed for only a few experiments each, the complete assemblies represent developments resulting from the study of a considerable number of different reactions in this Laboratory and are described in detail on account of their wide applicability in fields outside the scope of this paper.

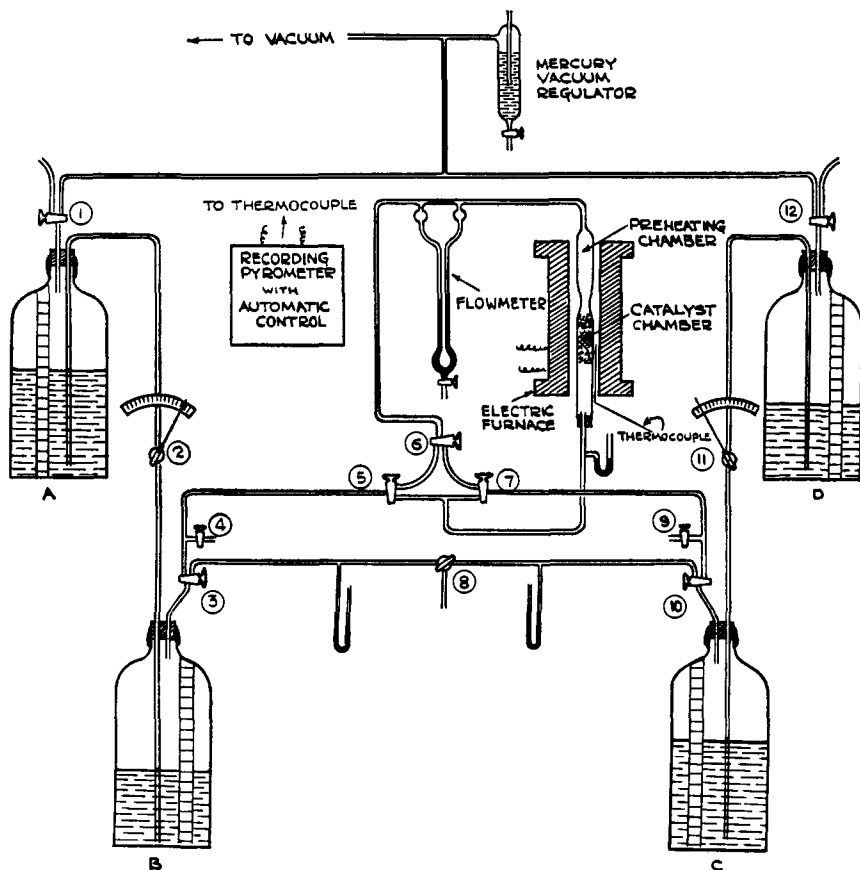


Fig. 1.—Apparatus for the hydrogenation of simple alkenes.

Figure 1 represents the apparatus used for the hydrogenation of alkenes. It was constructed entirely of glass, the various members being connected by an arrangement of stopcocks whereby the gas mixture could be passed between two calibrated gas-holders without the use of a circulating pump. After the first pass the direction of flow between storage bottles was reversed without change in direction of gas passage over the catalyst. Saturated salt solution was used as a retaining liquid. Gas was made to enter the receiving bottle by drawing the brine into an auxiliary storage bottle by use of reduced pressure, the rate being adjusted by setting Stopcocks 2 or 11, depending on the direction of flow, to give the desired setting on the Venturi flowmeter. The catalyst chamber was electrically heated, the temperature being automatically controlled by a Leeds-Northrup controller-recorder.

In the experiments recorded in Table I, 20 cc. of catalyst was used, which was reduced for two hours with hydrogen at the operating temperature prior to attempting the hydrogenation. Two passes of 5-7 liters of gas mixture were made, each pass requiring about one hour. In representative experiments complete gas analyses were made on a Fisher Universal Gas Analyzing Apparatus before the first pass and after the second one.

Figure 2 shows the device used in the atmospheric-pressure, high hydrogen-ratio experiments. Hydrogen was passed over 20 cc. of catalyst at the rate of about 10 liters per hour. Acetone was introduced into the hydrogen by entrainment, by passing the gas through a T, one leg of which dipped into the liquid. The concentration in the gas was determined by weighing the acetone loss and was regulated by altering the level in the T-tube. The products of reaction were separated from the large excess of hydrogen by use of a liquid-air trap followed by an activated charcoal scrubber.

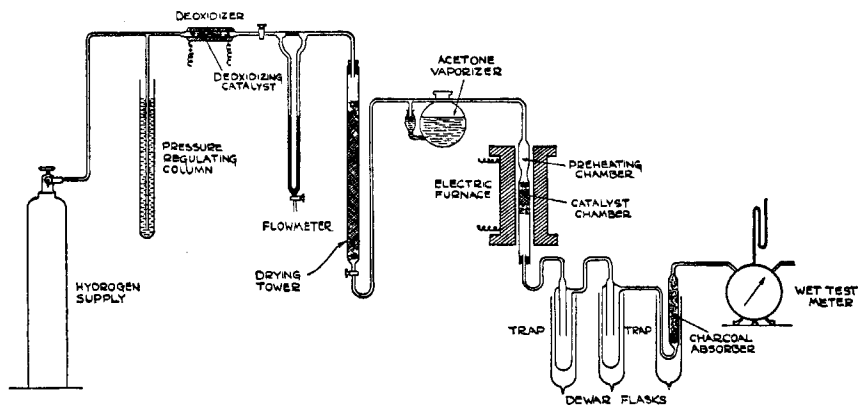


Fig. 2.—Apparatus for atmospheric pressure hydrogenation of acetone.

In carrying out the hydrogenation under high pressure acetone was pumped through a vaporizing vessel and thence over 50 cc. of catalyst at the rate of about 720 cc. per hour. At the inlet to the reaction tube the acetone vapor was joined at a T by a stream of hydrogen flowing from a high-pressure storage cylinder. Figure 3 shows details of the apparatus. The tubes, valves, and fittings were standard and were of the type frequently described in papers dealing with ammonia and methanol syntheses. The small, two-cylinder hydraulic pump used for injecting acetone was operated on a by-pass at a pressure slightly greater than the operating pressure, the rate being measured by buret readings and controlled by adjusting the valve feeding the reaction system. The flow of hydrogen was controlled by expanding the gas from a cooled trap through a flowmeter placed at the end of the system. During four hours the pressure dropped from 3000 to 1500 lb. per sq. in. The rate of hydrogen flow was about 1100 liters N. T. P. per hour. The liquid products were separated from the excess gas under pressure and were identified by fractional distillation.

Materials.—Ethylene and hydrogen were procured from the usual commercial storage cylinders and, except for drying as indicated in the several apparatus diagrams, were used without further purification. The hydrogen analyzed 99% and the ethylene was 98.2% absorbed in fuming sulfuric acid. In all reduction experiments care was taken to eliminate oxygen by use of hot copper or alkaline pyrogallol. The acetone was a redistilled, close-cut fraction from technical grade material. Propylene and butylene were prepared by catalytically dehydrating isopropyl and normal butyl alcohols over an alumina catalyst.

Catalyst Preparation.—The catalysts were prepared by well-known methods which have previously yielded highly active preparations when tested for the catalytic decomposition of alcohols. A suitable physical form was obtained by briquetting the dry powders and crushing the tablets to 8–14 mesh granules. Oxides of zinc, manganese, and magnesium were prepared by ignition of the pure oxalates at 400–450°. The first two of these were also prepared by precipitating the hydroxides with ammonium hydroxide. The oxides of vanadium and molybdenum were prepared by igniting ammonium vanadate and molybdate, respectively. Titania was prepared by precipitation of a solution of titanium potassium oxalate with ammonium hydroxide and washing the precipitate until free from alkali salts. The zinc oxide–chromium oxide catalyst was prepared by carefully reducing basic zinc chromate at 275°, in a stream of hydrogen.

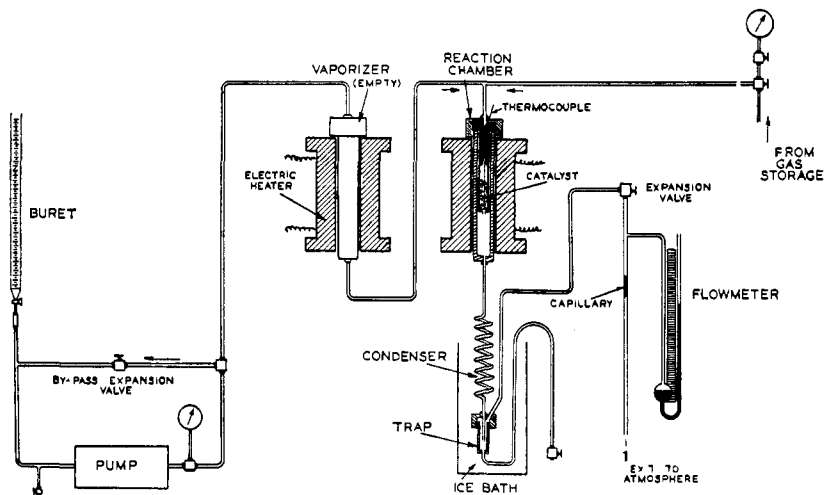


Fig. 3.—Apparatus for high pressure hydrogenation of liquids.

Alkali was introduced into a sample of this catalyst by moistening the washed and dried chromate with a solution of sodium carbonate prior to ignition. The iron-containing catalyst was prepared by spraying the requisite amount of a standard ferric chloride solution on zinc oxide (*ex-oxalate*), cadmium being introduced into another sample in the same way. Zinc hydroxide and aluminum hydroxide were co-precipitated with ammonium hydroxide, dried and ignited. The reduced copper catalyst was prepared by fusing copper oxide and reducing at 150°. Metallic zinc was deposited on zinc oxide (*ex-oxalate*) by placing a quantity of the metal in a tube adjacent to, but out of contact with the oxide. Hydrogen was passed over the heated metal and oxide, and the temperature gradient of the tube was so adjusted that condensation of zinc vapor took place on the somewhat cooler zinc oxide.

Reduction of Zinc Oxide.—Ten grams of briquetted zinc oxide (*ex-oxalate*) was reduced for fifty hours with dry, oxygen-free hydrogen at 500°, the rate of hydrogen flow being about 5 liters per hour. At the end of the specified time the catalyst was distinctly gray and a band of crystalline metallic sublimate had formed on the tube wall at the exit end of the furnace.

Summary

A comprehensive investigation has been made of the capacity of difficultly reducible, dehydrogenating oxides for catalyzing the hydrogenation

of simple alkenes. No reaction has been observed. Promoters such as chromium oxide and aluminum oxide which are suitable for activating the oxides for other reactions have failed to cause any manifestation of activity. On the other hand, the reaction proceeds smoothly when a metallic zinc or copper catalyst is employed. An active zinc-on-zinc oxide catalyst has been prepared by reducing zinc oxide in dry hydrogen.

Acetone has been hydrogenated over a zinc oxide-chromium oxide catalyst at atmospheric and elevated pressures, and other examples of the hydrogenation of compounds containing unsaturated oxygen atoms over oxide catalysts have been reviewed for the purpose of establishing the general proposition that oxide surfaces are capable of catalyzing the hydrogenation of compounds containing this kind of unsaturation while incapable of hydrogenating carbon-carbon unsaturation. Sodium carbonate has been found to be an effective agent for repressing the dehydration of isopropanol formed by the pressure hydrogenation of acetone.

An explanation of the specificity of catalytic oxides in the hydrogenation of organic compounds has been given, based on the idea that the degree of unsaturation of metal atoms in the surface of metallic compounds requisite for catalytic activity is conditioned not only by the degree of isolation of the active metal atoms but by the chemical nature of the surrounding atoms in the crystal lattice. Whether reaction is possible or not may depend likewise on the relative negativity of the unsaturated groups contained in the organic compound subjected to hydrogenation.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

KINETICS OF THE THERMAL CHLORINATION OF METHANE¹

BY ROBERT N. PEASE² AND GEORGE F. WALZ³

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It is well established, more particularly in the patent literature, that methane-chlorine mixtures undergo reaction in the neighborhood of 400° without the intervention of contact agents.⁴ When methane is in excess the reaction is rapid but non-explosive, and a mixture of methyl chloride,

¹ This paper contains results of an investigation carried out as a part of Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the American Petroleum Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor of Princeton University is Director of Project No. 7.

² Research Associate, American Petroleum Institute.

³ Research Assistant, American Petroleum Institute.

⁴ For example, Lacy, U. S. Patent 1,111,842 (Sept. 29, 1914); Schleede and Luckow, *Ber.*, **55**, 3710 (1922). For bibliography, see Egloff, Schaad and Lowry, *Chem. Rev.*, **8**, 1 (1931).