analysis of the partially effloresced product, while Col. B gives the analysis on a phosgene-free basis.

A repetition of the vapor-tension measurements made by Germann and Gagos has verified the composition of the phosgenate as containing two molecules of phosgene: $CaAl_2Cl_8.2COCl_2$. The vapor tension of the phosgenate at 25°, at which the measurements were carried out, is about 40 mm., which agrees with the value 25–30 mm. at 19°, found by them. The solubility of the completely dephosgenated salt at 25° was found to be 33 g. of salt per 100 g. of saturated solution, or 100 g. of the crystallized diphosgenate per 100 g. of solvent.

We wish to thank the Chemical Warfare Service for their interest in this work and for supplies of phosgene.

Summary

A method for the preparation and analysis of phosgeno salts in phosgene solution has been described, with particular reference to the calcium salt; the method is applicable to any soluble salt, not only in phosgene, but in other volatile solvents, where isolation from the atmosphere is essential, and where the pressures developed are not too great.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THIN FILMS OF PLATINUM AND NICKEL AND CATALYTIC ACTIVITY

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For some time there has been considerable discussion in the literature as to whether the active material in a nickel catalyst is in reality metallic nickel or an oxide or sub-oxide of some type.[2] As it is impossible to prepare a nickel catalyst from nickel oxide, which will be completely reduced, the study of this question by direct experiment has been limited to attempts at preparing catalysts from compounds of nickel containing no oxygen. Since the importance of extent of surface has seemed to be so great, the author believed it possible to prepare a finely-divided catalyst which should have an exceedingly large surface and yet by virtue of its method of preparation be entirely free from oxygen or oxide. He proposed to prepare such a material (nickel) and investigate its catalytic activity for the reaction, $C_2H_4 + H_2 \longrightarrow C_2H_6$.

[1] National Research Fellow in Chemistry.

[2] Kelber, *Ber.*, **54**, 1701 (1921). Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 113 (1921). Boswell, *Proc. Roy. Soc. Canada*, **16**, sect. III (1922).

Preparation of Gases

Hydrogen was prepared by the method of Morley.[3] It was generated by electrolysis of a solution of distilled sulfuric acid in distilled water. The gas was purified by passage through a train consisting of the following materials: concd. potassium hydroxide solution, concd. sulfuric acid, solid potassium hydroxide, hot copper turnings, sulfuric acid on pumice and phosphorus pentoxide. No trace of oxygen could be determined by the ferrous-pyrocatechol method.[4] The gas was then stored in a glass bulb that had previously been baked and evacuated at 450° for 48 hours. The ethylene was prepared by fractional distillation of commercial ethylene (99% pure). It was also stored in a bulb that had been baked and evacuated at 450° for several days.

Preparation of the Catalyst

A tungsten filament was cleaned by means of fused sodium nitrite and then electroplated with nickel, using a Kahlbaum nickel electrode and a solution[5] of 562 g. of nickel sulfate, 16.8 g. of sodium fluoride and 62.0 g. of boric acid in 2 liters of water. This filament was immediately coated with naphthalene and sealed into a bulb as shown in Fig. 1. The bulb was connected with another bulb B containing Pyrex glass wool. The whole tube was baked out and evacuated at a temperature of 450° for 72 hours. The upper part of the tube, containing the tungsten-nickel filament, was then maintained at a temperature of several hundred degrees, while the lower bulb, containing the glass wool, was immersed in liquid air. A heavy current was sent through the filament, causing the nickel to evaporate. The nickel was deposited on the glass wool in the bulb immersed in liquid air. This bulb was then sealed from the filament part of the tube, and utilized in the experimental work.

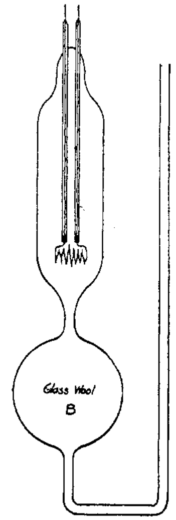

Fig. 1.—Reaction tube for preparing metals of large surface.

Procedure

The mixture of gases containing 20% of ethylene was passed through a sodium-potassium alloy in order to remove the final traces of oxygen and water vapor, and admitted into the bulb containing the catalyst. No reaction could be observed at any temperature up to 200°, indicating that the metal had no catalytic activity for the dried and purified gases; 1% of pure oxygen was next admitted to the reaction chamber. Again no reaction could be observed. It was then thought that possibly water vapor, which is essential in many reactions, might also be necessary in this one. A few per cent. of water vapor was therefore admitted into the reaction bulb. As before, no reaction could be observed. The author was therefore forced to the conclusion that a nickel catalyst could not be prepared by this method, regardless of the extent of the surface. In order to determine whether this condition was peculiar to nickel or not, the same procedure was carried out and a platinum film deposited on glass wool in exactly the same manner as with nickel. In this case also, all the results were negative.

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[3] Morley, *Z. physik. Chem.*, **20**, 243 (1896).

[4] Latimer, Buffington and Hoenshel, THIS JOURNAL, **47**, 1571 (1925).

[5] The author wishes to thank Dr. Max Knobel for supplying him with the solution.

Dr. H. H. Storch has since questioned whether it is possible to remove all adsorbed gases from glass surfaces by heating and pumping. The possibility, therefore, remains that sufficient oxygen molecules may have been left on the glass wool to give nickel oxide rather than a nickel film. The author is not so situated as to be able to test this, unfortunately, but is inclined to believe that it is a possibility rather than a probability because of the amount of nickel involved and the fact that no reduction in volume, indicating reduction of oxide by hydrogen, occurred at 200°. However, it must be admitted as a possibility.

Since this work was completed, Adkins[6] has published the results of an investigation indicating that the catalyst is nickel and not nickel oxide, and Kelber[7] has prepared active catalysts from nickel compounds that contain no oxygen.

Discussion of Results

As a result of these experiments, the author believes that the importance of the extent of surface as we ordinarily mean a surface, has been much overestimated. There is an inherent difference in the nature of a metallic catalyst which results from the method of its preparation. It is quite likely that the mechanism of preparing these films by an evaporation from a heated surface in a vacuum involves the throwing off of molecules or groups of molecules of the metal. These molecules will have the same electronic configuration that they have in the bulk metal. This is not necessarily true in the case of a catalyst prepared, say, by reduction of the oxide at low temperatures. Here we know that the catalytic activity, for example, can be destroyed by heating to temperatures somewhat higher, it is true, than those at which the reduction takes place, but very much lower, nevertheless, than the melting point of the metal. It seems not at all unlikely that a catalyst may have electrons that are on somewhat different energy levels than in the case of the crystalline metal. The so-called active surface of the catalyst consists, therefore, of those molecules that have electrons in these outer energy levels.

It appears that the future holds in store for us something of the following type of solution for these problems. In the generalized reaction, $A + B = C$, let us assume that the valence electrons in A, B and C are in certain energy levels N_1, N_2, N_3, respectively. Then let us postulate that electrons can only go from their respective energy levels to new levels that are but one unit removed from the old. This means that there is a certain selectivity in the changes in levels, and that such changes must occur in single steps. In the reaction given above, therefore, we cannot go from A with valence electrons in N_1 directly to C with valence electrons in N_3, even though the free-energy data indicate that reaction should occur. A catalyst is necessary and we assume that D with valence electrons in N_3 forms DA with the electrons in N_2 where the changes have occurred

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[6] Adkins and Lazier, This Journal, **46**, 2291 (1924).

[7] Kelber, *Ber.*, **57B**, 142 (1924).

in single unit levels. Now the reaction immediately goes forward.

$$AN_1 + DN_3 = D{:}AN_2;\ D{:}AN_2 + BN_2 = CN_3 + DN_3$$

In this connection it is interesting to mention the work of Caro and Franck[8] who found that excited mercury atoms (they utilized sufficient energy to get the first resonance of mercury) can dissociate hydrogen molecules upon impact. This means that the resonated mercury atoms can transfer their extra energy to the hydrogen molecules, which we may consider a case represented by the formation of DA in the equation above.

Applying the same ideas to radiant-energy catalysis we assume the intermediate step to be $AN_1 + xh\nu = AN_2$, and the latter are the activated molecules.

The theory makes no assumptions with regard to actual structure. It should, therefore, apply equally to static and dynamic models.

When we consider the character of solid catalysts from this point of view, the fact that they are in the main elements of high atomic number has considerable significance. Since large numbers of electrons are concerned, the energy differences between the various levels in the outer rings, shells or orbits are not large. In fact, for this very reason it is extremely difficult to fix the position of the outer electrons from spectral data. A dynamic equilibrium must exist in these elements between atoms with valence electrons in various energy levels. Hence we have the phenomenon of passivity; in the passive form there exists a predominance of atoms of low energy content or some sort of more stable arrangement of electrons, whereas in the active form the situation is reversed. In the preparation of the catalyst the equilibrium is frozen while the atoms of high energy predominate. The fact that these elements form colored compounds may be taken as additional evidence that the jump between different energy levels is not large.

The variation in catalytic activity with mode of preparation of a given catalyst depends, therefore, on the number of atoms containing electrons in higher energy levels. Incidentally this accounts also for the fact that the various samples of nickel catalyst prepared at Princeton last year by Taylor and Beebe[9] showed different heats of adsorption for hydrogen. Furthermore, on the basis of these ideas the heat of solution of an active nickel catalyst should be greater than that of crystalline nickel. This it is proposed to test experimentally.

Specificity in catalysis may be explained by the assumption that the energy-level steps are different in the different reactions and the necessary steps for the transition from A to C may be provided by Catalyst D, whereas we need Catalyst F to provide the proper steps for the change from A to E.

De-activation by heating is a case where the atoms of high energy con-

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[8] Caro and Franck, *Z. Physik*, **11**, 161 (1922).

[9] Beebe and Taylor, THIS JOURNAL, **46**, 43 (1924).

tent go over to atoms of low energy content. De-activation of this type should affect adsorption of all reactants in very nearly the same degree. On the other hand, when we use a poison such as the mercury used by Dr. Pease[10] in his experiments with ethylene and hydrogen we have an entirely different case. Here reaction between the mercury atoms and certain of the nickel atoms may take place and those atoms have probably exerted a specificity in their adsorption. Dr. Pease has shown the following decreases in adsorption of hydrogen and ethylene by two samples of copper de-activated in the above two ways.

	Mercury-poisoned copper		Copper de-activated by heating		
	760 mm.	100 mm.	700 mm.	100 mm.	
H_2	3.40	5.00	2.60	2.0	from his curves
C_2H_4	1.60	1.90	1.95	1.3	

Although the percentage decreases, 92% for hydrogen and 14% for ethylene in the case of mercury poisoning and 70% for hydrogen and 22% for ethylene, offer nothing quantitative in support of these views, it is first to be remembered that they represent adsorption at one atmosphere pressure and therefore include both primary and secondary adsorption. A comparison of the absolute values does show an approach toward the same order of magnitude in the case of de-activation by heating. To test these views properly a distinction must be made between primary and secondary adsorption, for it is only the former type which comes into question. This does not seem possible from his data. It is interesting to note that both Pease[10] and Benton[11] conclude that it is this type of adsorption that is related to the catalytic activity of the catalyst.

This work was performed while the author was a National Research Fellow in Chemistry. This opportunity is taken to express his thanks to the National Research Council.

Summary

Thin films of platinum and nickel were prepared by evaporation in a vacuum and condensation on Pyrex glass wool in a tube immersed in liquid air.

No reaction was observed when these films were tested for catalytic activity in the reaction $H_2 + C_2H_4 = C_2H_6$. The films were not catalytically active whether oxygen or water vapor was absent or present.

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[10] Pease, THIS JOURNAL, **45,** 2296 (1923).

[11] Benton, *ibid.,* **45,** 900 (1923).