Of the three absorption bands of $Cr(H_2O)_6^{+3}$ only the lowest energy state is considered, since it is assumed that there is quite rapid internal conversion from the higher states. This assumption is consistent both with previous fluorescence studies,[8] and with the observation that in the present case, the quantum yield does not depend upon which absorption band is irradiated. Such an estimate for the lowest energy band is 1.4×10^{-5} sec., which should correspond to the mean life of that state if the only mode for return to the ground state is direct fluorescence. The lack of fluorescence indicates that the actual lifetime of this state is many orders of magnitude less; in fact, too short for any detectable reaction to occur. However, the life time of electronic excitation may actually be much longer than the lifetime of the lowest excited quartet state. According to the spectral assignment of Finkelstein and Van Vleck for solid chrome alum,[13] there is a doublet state which lies fairly close to the lowest excited quartet state. If before conversion to the ground state, some of the excited $Cr(H_2O)_6^{+3}$ passed into such a spin forbidden state of long life time, it could well have sufficient time to undergo the chemical exchange reaction while still electronically excited.

Acknowledgment.—The authors would like to thank their colleagues for many helpful discussions concerning the interpretation of the results. We are especially indebted to Prof. R. Bersohn and Dr. A. C. Albrecht.

[13] R. Finkelstein and J. H. Van Vleck, *J. Chem. Phys.*, **8**, 790 (1940).

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Mechanism of Chemisorption: Ethylene and Ethane on Nickel

BY P. W. SELWOOD

RECEIVED AUGUST 23, 1956

Magnetization–volume isotherms have been obtained for ethylene and for ethane on a commercial nickel–kieselguhr catalyst, and for ethylene on a coprecipitated nickel–silica catalyst. Isotherms have also been obtained for hydrogen on a nickel surface already covered in part with chemisorbed ethylene, and for ethane on a surface already covered with hydrogen. It has been shown that if the d-band of the nickel in these catalysts gains one electron per chemisorbed hydrogen atom, the d-band gains on the average a little over two electrons for each ethylene molecule chemisorbed at room temperature. Admission of ethylene to nickel at higher temperatures is followed by dissociative adsorption or fragmentation. On a coprecipitated catalyst at 100° this fragmentation yields approximately a six-electron transfer per molecule of chemisorbed ethylene. Ethane at room temperature is chemisorbed on a bare nickel surface with somewhat more than a six-electron gain by the nickel per molecule of ethane. Ethane is not chemisorbed on a nickel surface already covered with hydrogen. In these catalyst systems there are three or four times as many nickel sites available to hydrogen as to ethylene, and over six times as many to hydrogen as to ethane. Admission of hydrogen to a nickel surface already covered with ethylene leads both to the formation of ethane and to the chemisorption of hydrogen.

The purpose of this work was to extend the method of magnetization–volume isotherms to ethylene, to ethane, and to certain aspects of the ethylene hydrogenation reaction.[1]

Experimental

All the results reported below were obtained by the induction method previously described.[1] Adsorptions were made and magnetizations were measured at 27° except as otherwise stated.

Two catalyst samples were used. One was Universal Oil Products Company nickel–kieselguhr hydrogenation catalyst, containing 52.8% nickel. This catalyst has an approximate surface area (B.E.T., N_2) of 175 sq. m. per g. The other catalyst was a coprecipitated nickel–silica prepared as described by Van Eyk Van Voorthuisjen and Franzen,[2] and designated by them CLA 5421. This sample contained 37.5% nickel, and had a surface area of about 200 sq. m. per g. Specific magnetization *vs.* temperature for samples similar to these already have been published.[1]

Each sample was reduced in flowing hydrogen before each series of measurements. Reduction was at 360° for 12 hr., followed by evacuation at 10^{-6} mm. for 1 hr. at 360°, and cooling *in vacuo* to 27°.

Hydrogen used for reduction and for adsorption measurements was purified as previously described,[1] as was the helium used for dead-space determination. The ethylene was Phillips Research Grade guaranteed to be 99.9+% pure. The ethane was Mathieson Technical Grade.

The results reported below were obtained on samples weighing 6 to 8 g.

Results

Figure 1 shows automatically recorded changes of magnetization observed when ethylene was flushed over evacuated U. O. P. catalyst, up to atmospheric pressure. The change is negative, that is, in the same direction as that caused by chemisorbed hydrogen on nickel at room temperature. The effect is, however, considerably smaller than that for hydrogen. This accounts for our failure to observe the effect for ethylene at room temperature in our first experiments in which the less sensitive Faraday method was used.[3] We did observe and report the effect of ethylene at higher temperatures, as described below.

It will be seen that there is a fairly large thermal transient caused by the heat of chemisorption. After temperature equilibrium had been reached the sample was evacuated with the result shown, namely, a small positive transient appeared. No permanent change of magnetization was produced by evacuation even though, as will be shown below, over half the ethylene was thus removed. This result merely shows, as is well known, that a large fraction of the ethylene adsorbed on nickel–silica at room temperature is held by van der Waals forces.

Figure 2 shows both magnetization–volume isotherms and, the more familiar, pressure–volume iso-

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[1] P. W. Selwood, THIS JOURNAL, **78**, 3893 (1956).

[2] J. J. B. Van Eyk Van Voorthuisjen and P. Franzen, *Rec. trav. chim.*, **70**, 793 (1951).

[3] P. W. Selwood, S. Adler and T. R. Phillips, THIS JOURNAL, **77**, 1462 (1955).

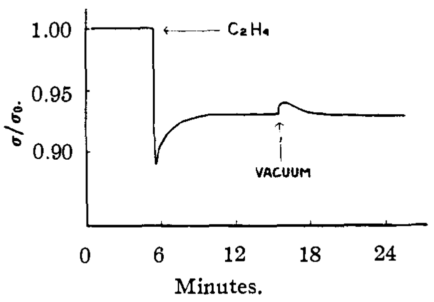

Fig. 1.—Automatic recording of magnetization changes during admission and evacuation of ethylene on nickel-kieselguhr.

therms for hydrogen on a U. O. P. catalyst sample. The result is similar to that already described for hydrogen on nickel,[1] but is needed here in connection with interpretation of the new results on ethylene hydrogenation.

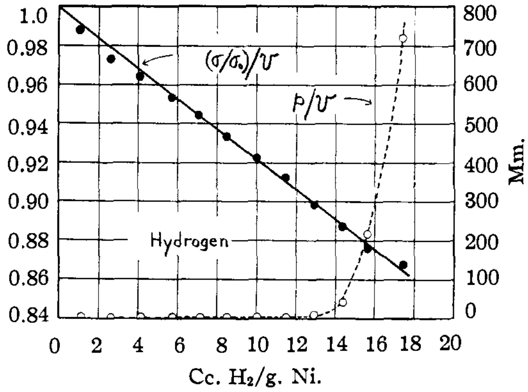

Fig. 2.—Magnetization–volume and pressure–volume adsorption isotherms for hydrogen on nickel-kieselguhr at 27°.

In Fig. 3 there are shown the results for ethylene adsorption on U. O. P. catalyst. After atmospheric pressure had been reached the sample was evacuated for 15 minutes. This resulted in the removal of considerable gas but with no change of magnetization. After a few minutes pumping no further gas could be removed, at room temperature. The volume of residual ethylene was then found by adding ethylene again up to atmospheric pressure. The total volume of ethylene first adsorbed was 10.8 cc. (S. C.) per g. of nickel. The volume taken up in the second addition was 6.0 cc. This was taken to mean that 4.8 cc. of ethylene remained chemisorbed on the sample. The second addition of ethylene caused no change of magnetization and was thereby proved to be all physical adsorption.

This procedure for finding the volume of residual chemisorbed ethylene ignores the fact that certain reactions may take place in this system at room temperature. One possibility is that of polymerization. But under the conditions and short time (15 min.) of the experiment it is hard to believe that polymerization could have introduced any serious error. Another possibility is that of self-hydrogenation. This, if occurring to any appreciable degree, could seriously impair the interpretations given below. The desorbed gas was therefore analyzed by absorption in bromine water. It was

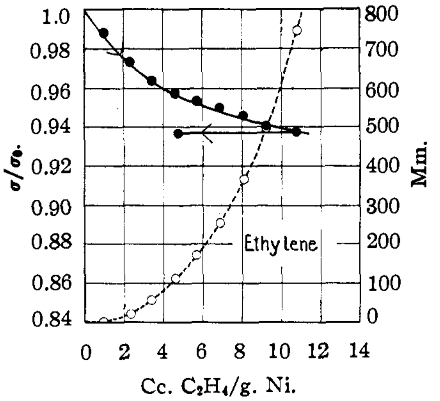

Fig. 3.—Magnetization–volume and pressure–volume adsorption isotherms for ethylene on nickel-kieselguhr at 27°.

found that no saturated hydrocarbon was present in sufficient amount to warrant consideration for the purposes of this work.

Two further points may be mentioned. All the adsorption results reported here are given for convenience in cc. of gas adsorbed (S. C.) per g. of nickel. It will be understood that the silica support must contribute to the van der Waals part of the total adsorption. The other point is that one may wonder why more ethylene cannot be pumped off if the pressure at 4.8 cc. residual ethylene is actually over 100 mm. as seems to be indicated in Fig. 3. But this was doubtless due to hysteresis in the desorption isotherm. The actual pressure at 4.8 cc. ethylene after desorption was very small.

Figure 4 shows the results for a hydrogen isotherm *over* the 4.8 cc. of chemisorbed ethylene, on the same sample as for Fig. 3.

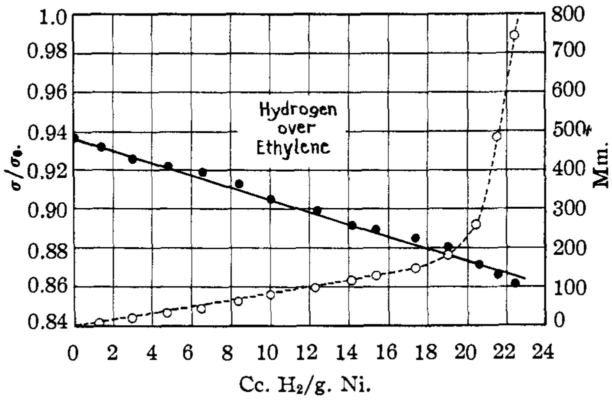

Fig. 4.—Magnetization–volume and pressure–volume isotherms for hydrogen on nickel-kieselguhr already partially covered with chemisorbed ethylene at 27°. The p–v isotherm shown has not been corrected for the modest amount of ethane present in the gas phase at the higher pressures.

In view of the rather unexpected result shown in Fig. 4, namely, that hydrogen may in fact be chemisorbed on a nickel surface already covered (so far as possible) with chemisorbed ethylene, this experiment was repeated on the coprecipitated catalyst. The results were qualitatively the same as shown in Fig. 4. The volume of chemisorbed ethylene, being in this case determined by removal of the excess by exhaustion through a Toepler pump, was 5.0 cc. per g. of nickel, the volume of hydrogen taken up to atmospheric pressure in the absence of ethylene was 22.0 cc., and in the presence of the ethylene 27.0 cc. Coprecipitated catalysts are subject to a very large magnetic change on exposure to hydrogen. For this catalyst the effect for hydrogen was the largest so far observed, namely, 48%.

Figure 5 gives ethane isotherms on a bare U. O. P. nickel surface, and Fig. 6 shows ethane isotherms on the same nickel on which about 12.5 cc. of chemisorbed hydrogen already was present. This last isotherm was obtained by first adding hydrogen up to atmospheric pressure over the bare catalyst, then pumping out for 15 min., that is, until the hydrogen pressure was a fraction of a mm. The ethane was then added in successive increments in the usual way.

Fig. 5.

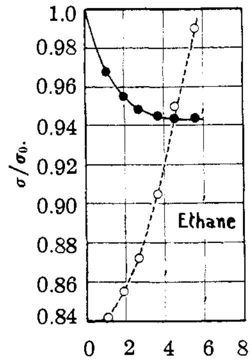

Fig. 6.

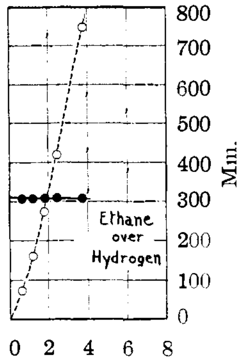

Fig. 5.—Magnetization-volume and pressure-volume adsorption isotherms for ethane on nickel-kieselguhr at 27°.

Fig. 6.—Magnetization-volume and pressure-volume adsorption isotherms for ethane on nickel-kieselguhr already covered (in part) with chemisorbed hydrogen, at 27°.

Conclusions to be drawn from the data shown in Figs. 3 and 4 are in disagreement with certain current views concerning the reactivity, or fragmentation, of chemisorbed ethylene. For this reason a series of experiments was performed in which ethylene was admitted to the coprecipitated catalyst held at 100°. Typical recorded results of this experiment are shown in Fig. 7. In the run shown, 6.2 cc. ethylene per g. nickel was admitted. The pressure rose quickly to 159 mm. and, except for a slight increase, remained steady over several hours. It will be noted that the results obtained in this experiment are in sharp contrast to those in which the ethylene is admitted to the nickel at room temperature, even though the quantity of ethylene chemisorbed in these cases is very nearly the same.

At the conclusion of the run shown in Fig. 7 the sample was cooled to 27°, evacuated to remove excess ethylene, and treated with hydrogen. The hydrogen uptake to atmospheric pressure was only 20.6 cc. and the magnetization fell to $\sigma/\sigma_0 = 0.58$.

Discussion

In a previous paper[4] we showed that the magnetization results are, in general, consistent with the idea, often expressed, that each chemisorbed hydrogen atom contributes one electron to the nickel particle to which it becomes attached. The possible complication that hydride ions are formed on extremely small nickel particles does not greatly concern us on the catalysts and in the temperature range under study in the present investigation. It will be assumed that the slope of the magnetization-volume isotherm for hydrogen shown in Fig. 2 is, therefore, a measure of the adsorption condition in which the ratio of atoms chemisorbed to electrons gained by the nickel is unity. This view is in agreement with current ideas concerning the adsorption of hydrogen on palladium. If, however, it should be shown that formation of the Ni–H bond does not involve a one-electron gain by the d-band of the nickel, the conclusions drawn below will nevertheless be valid provided that formation of the Ni–C bond produces the same magnetic change as does the Ni–H bond. That this is a reasonable assumption is supported by consideration of the magnetic properties of coördination complexes involving metal–carbon bonds.

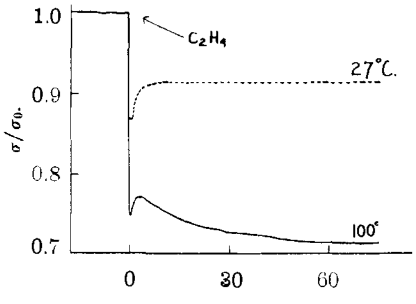

Fig. 7.—Automatic recording of magnetization changes during admission of ethylene on nickel–silica at 100°, as compared with admission at 27°.

It will be noted that the initial slope of the magnetization isotherm shown for ethylene in Fig. 3 is a little larger than that for hydrogen. This is to say that the nickel gains on the average a little more than two electrons for every ethylene molecule chemisorbed. This is clear confirmation for the view that ethylene is, in the system studied, held principally by two-site attachment,[5] and that a moderate fraction of the ethylene dissociates hydrogen to occupy four or more sites—two for the dissociated hydrogen and two or more for the acetylenic residue.

One sees, however, that additional increments of ethylene have a smaller effect on the magnetization. It might be surmised that this is due to one-site attachment, but the easy removal of over half of the ethylene with no attendant change of magnetization shows clearly that a substantial fraction of the ethylene is held by van der Waals forces. The actual fraction of physically adsorbed ethylene at one atmosphere pressure is 55.5%.

It will be noted that the volume of chemisorbed ethylene is much smaller than the volume of hydrogen which may be adsorbed on the same catalyst. This observation has been made several

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(4) L. E. Moore and P. W. Selwood, THIS JOURNAL, **78**, 697 (1956).

(5) J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934); see also M. E. Winfield, *Australian J. Sci. Res.*, **A4**, 385 (1951).

times in the past, as has the implication that there are at least two kinds of nickel surface sites.[6,7] One class of sites is accessible to ethylene or to hydrogen, another class of sites is accessible to hydrogen alone. The actual fraction of sites accessible to ethylene is not readily determined with precision because hydrogen apparently is chemisorbed completely at pressures of one atmosphere and possibly higher. We believe it correct to say that, in the system studied here, there are approximately three sites accessible to hydrogen for every one accessible to ethylene. All the conclusions drawn for the U. O. P. catalyst are equally valid for the coprecipitated catalyst except that for the latter there are three and a half to four sites accessible to hydrogen for every site accessible to ethylene.

Turning now to the hydrogen isotherms obtained on a nickel surface already saturated with chemisorbed ethylene, as shown in Fig. 4, it will be seen that a very large volume of hydrogen is taken up. But, the total hydrogen taken up at one atmosphere pressure is 4.9 cc. greater than the volume of hydrogen adsorbed on a bare nickel surface at one atmosphere. This excess volume of hydrogen is the same as the volume of chemisorbed ethylene present. There can be little doubt that the excess hydrogen is used in the expected fashion to hydrogenate the ethylene, and this is confirmed by the appearance of ethane in the gas phase.

It is, of course, far from surprising to find that hydrogen reacts with ethylene to form ethane over a nickel catalyst. But if the fraction of hydrogen used in hydrogenation is actually 4.9/22.2 as indicated in Figs. 2 and 4, then after the addition of, say, 12 cc. of hydrogen the volume of ethane liberated should be 12 cc. $\times$ 4.9/22.2 = 2.6 cc. In a dead-space of 8.6 cc. this should exert a pressure of 230 mm., whereas the actual pressure was only 100 mm.

In the above calculation it has been assumed that the product ethane is not adsorbed. Turning to Figs. 5 and 6, one sees that while ethane is chemisorbed on a bare nickel surface it is not chemisorbed at room temperature in the presence of an adsorbed layer of hydrogen. Ethane is, however, physically adsorbed on such a catalyst surface at room temperature to the extent of almost 4 cc. per g. of nickel at one atmosphere. We have then a complete explanation for the pressure–volume isotherm shown in Fig. 4. After the addition of 12 cc. of hydrogen there has been formed 2.6 cc. of ethane. At a partial pressure of 100 mm. almost 1 cc. of this would be physically adsorbed. The remaining 1.6 cc. of ethane in 8.6 cc. dead space would exert a pressure of 140 mm., which is fairly close to that actually observed.

The above reasoning involves two assumptions: first, that the hydrogen is chemisorbed in more or less normal fashion in spite of the presence of ethylene and ethane and, second, that the hydrogen neither hydrogenates the ethylene preferentially nor is it adsorbed preferentially but rather that it reacts purely according to chance impact on the surface. Justification for these two assumptions follows.

The magnetization isotherm in Fig. 4 is a straight line with a negative slope. Yet replacement of a chemisorbed ethylene molecule by two atoms of hydrogen would produce either no change or a slight positive change of magnetization. There can, therefore, be no question that hydrogen is chemisorbed in the presence of ethylene. On the other hand, the regular increase of pressure with added hydrogen in Fig. 4 shows that the generation of ethane is linear with each increment of hydrogen. There seems little doubt that for approximately every four molecules of hydrogen taken up under the conditions of Fig. 4, one molecule is used to hydrogenate the ethylene.

Another observation in connection with Fig. 4 is that the slope of the magnetization isotherm is much less than that for the corresponding hydrogen isotherm shown in Fig. 2. It requires 2.4 atoms of hydrogen on a nickel–ethylene surface to lower the magnetization the same fraction as may be achieved by one hydrogen atom on a bare nickel surface. To express this in another way: if one electron is gained by the bare nickel for each hydrogen atom adsorbed, then one electron is gained by the nickel–ethylene surface for each 2.4 hydrogen atoms taken up.

The problem of interpretation now resolves itself into finding a structural relationship that will account for the following two observations: (1) the number of sites accessible to ethylene is only one-third of the number accessible to hydrogen, and (2) a net gain of one electron by the nickel during hydrogenation of ethylene requires 2.4 atoms of hydrogen.

Table I shows some possible configurations and mechanisms. Class (A) sites and class (B) sites are accessible to hydrogen; Class (A) sites alone are accessible to ethylene. The ratio e/H given in the table is the net gain of electrons by the nickel per atom of hydrogen taken up. It will be clear from Table I that situation (III) must be a close approximation to the truth. Of the sites accessible to hydrogen only one-third is accessible to ethylene, and the addition of eight atoms of hydrogen to such a surface yields a net gain of only four electrons. It will be recalled that the adsorption of ethylene as in Fig. 3 results in a little more than a two-electron gain by the nickel for each ethylene molecule adsorbed. If this modest correction is made then the ratio e/H for situation (III) in Table I is found to be almost exactly 1/2.4, as observed experimentally.

For the coprecipitated catalyst the corresponding figures for e/H are (before correction for some dissociation of the ethylene): calcd. 1.7 to 1.8; found, 2.2.

The conclusions drawn above are in sharp disagreement with the fact that the hydrogen–deuterium exchange reaction is strongly inhibited by the presence of chemisorbed ethylene on nickel, and the inference that hydrogen is not chemisorbed as atoms under these conditions.[6,8] None of the situa-

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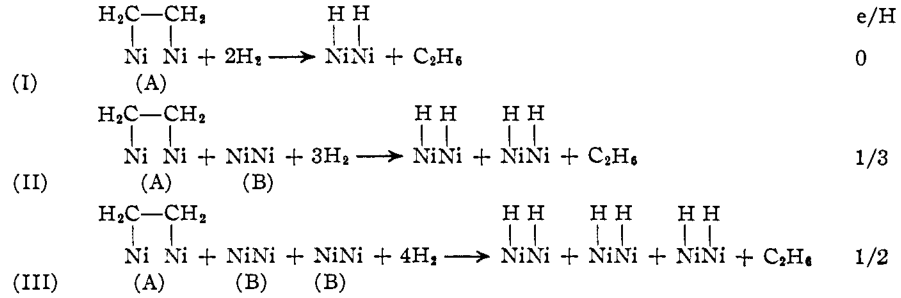
[6] G. H. Twigg and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A171**, 55 (1939).

[7] O. Beeck, A. E. Smith and A. Wheeler, *ibid.*, **A177**, 62 (1940).

[8] This poisoning effect of ethylene has been confirmed amply by several workers.

TABLE I

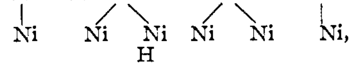
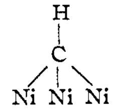
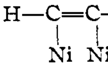
NET ELECTRON GAIN PER HYDROGEN ATOM TAKEN UP, FOR THREE DIFFERENT NICKEL–ETHYLENE SURFACE CONFIGURATIONS



		e/H
(I)	$\underset{\text{(A)}}{\begin{matrix}H_2C{-}CH_2\\ \vert\quad\ \vert\\ Ni\ \ Ni\end{matrix}} + 2H_2 \longrightarrow \begin{matrix}H\,H\\ \vert\ \vert\\ NiNi\end{matrix} + C_2H_6$	0
(II)	$\underset{\text{(A)}}{\begin{matrix}H_2C{-}CH_2\\ \vert\quad\ \vert\\ Ni\ \ Ni\end{matrix}} + \underset{\text{(B)}}{NiNi} + 3H_2 \longrightarrow \begin{matrix}H\,H\\ \vert\ \vert\\ NiNi\end{matrix} + \begin{matrix}H\,H\\ \vert\ \vert\\ NiNi\end{matrix} + C_2H_6$	1/3
(III)	$\underset{\text{(A)}}{\begin{matrix}H_2C{-}CH_2\\ \vert\quad\ \vert\\ Ni\ \ Ni\end{matrix}} + \underset{\text{(B)}}{NiNi} + \underset{\text{(B)}}{NiNi} + 4H_2 \longrightarrow \begin{matrix}H\,H\\ \vert\ \vert\\ NiNi\end{matrix} + \begin{matrix}H\,H\\ \vert\ \vert\\ NiNi\end{matrix} + \begin{matrix}H\,H\\ \vert\ \vert\\ NiNi\end{matrix} + C_2H_6$	1/2

tions represented in Table I could be expected to poison the nickel surface for the hydrogen–deuterium exchange.

Our results for the mode of attachment of ethylene on a bare nickel surface are also in apparent disagreement with those reported by Pliskin and Eischens,[9] who on the basis of infrared absorption studies found extensive fragmentation of the ethylene. These workers did, however, find results in agreement with those reported here for ethylene adsorbed on a nickel surface containing some chemisorbed hydrogen.

A clue to these discrepancies is found in the paper of Turkevich, *et al.*,[10] who found no poisoning by ethylene on nickel–kieselguhr at −78°, but marked poisoning on a nickel wire at 90°. This result suggests that some secondary reaction of the ethylene is responsible for the poisoning and this view is supported strongly by the results shown in Fig. 7. When ethylene is admitted to the catalyst at 100° the loss of magnetization is much greater than when admission is at room temperature. Furthermore, progressive fragmentation of the ethylene is readily followed for an hour or more until a steady state is reached corresponding to over six bonds to the nickel for every ethylene molecule adsorbed, instead of the two bonds found at room temperature. We have insufficient information to determine the nature of the adsorption complex formed at the higher temperature. The magnetic results are consistent with  $\overset{H}{\overset{\vert}{Ni}}\ \ \overset{H-C\text{———}C-H}{Ni\ \ Ni\ \ Ni\ \ Ni}\ \ \overset{H}{\overset{\vert}{Ni}}$, or with a mixture of two  $\overset{H}{\overset{\vert}{\overset{C}{Ni\ Ni\ Ni}}}$ four  $\overset{H}{\overset{\vert}{Ni}}$ and one  $\begin{matrix}H{-}C{=}C{-}H\\ \vert\quad\ \vert\\ Ni\ \ Ni\end{matrix}$, although carbon bonding to more than one nickel seems not to have been considered by Winfield.[4] It will be noted that after the fragmentation process had taken place the catalyst had lost some of its ability to adsorb hydrogen.

These results which demonstrate progressive fragmentation of the adsorbed ethylene clear up most of the difficulty mentioned above. When ethylene is admitted to bare nickel at low temperature it is adsorbed primarily by the familiar two-site attachment and in this way can exert little or no poisoning effect on the hydrogen–deuterium exchange reaction. As the temperature is raised fragmentation of the ethylene occurs; this results in increased occupation of nickel sites, and poisoning becomes marked. Whether or not poisoning becomes complete doubtless will depend on the initial ratio of sites accessible to hydrogen and to ethylene. The lower this ratio the more effective, it may be predicted, will poisoning become. Actually the coprecipitated catalyst on which fragmentation was demonstrated above was not the best choice to show this effect because the H_2/C_2H_4 ratio of accessible sites is fairly high.

In the work described here slight fragmentation of the ethylene was observed at room temperature, while extensive fragmentation is implied by the work of Eischens and by others. There is no real conflict here because the fragmentation process which is rapid at 100° must certainly occur also at room temperature. How much fragmentation occurs will depend on the intrinsic activity of the surface, on the time elapsed between admission of the ethylene and further testing of the surface (all room temperature experiments reported here were completed in less than one hour), and also on the rate of admission of the ethylene, the adsorption of which heats the nickel appreciably.

Pliskin and Eischens report evidence for the presence of adsorbed ethyl radicals on a sample to which first ethylene and then hydrogen was admitted. The results reported here do not deny this possibility. They do, however, require the added hydrogen to be used at random for hydrogenation and for chemisorption, and not for hydrogenation before chemisorption or *vice versa*. The results reported here are also not inconsistent with the view that ethylene is hydrogenated from the gas phase.

A few further conclusions may be drawn. From Fig. 5 it will be seen that the initial magnetization slope for ethane on bare nickel is twice that observed for ethylene and over four times that for hydrogen. The chemisorption of a molecule of ethane clearly involves a minimum four-site attachment, thus confirming the well-established dissociative mechanism for paraffin–deuterium exchange.[11] Actually the dissociation probably preceeds even further with some ethane molecules requiring six or more sites.

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(9) W. A. Pliskin and R. P. Eischens, *J. Chem. Phys.*, **24**, 482 (1956).

(10) D. O. Schissler, S. O. Thompson and J. Turkevich, International Congress on Catalysis, Philadelphia, Sept. 10–14, 1956. Preprint Lecture 6.

(11) K. Morikawa, W. S. Benedict and H. S. Taylor, THIS JOURNAL, **58**, 1445, 1795 (1936).

The total volume of ethane which may be chemisorbed appears (by comparison of Figs. 3 and 5) to be a little under half the volume of ethylene which may be chemisorbed. This result suggests that hydrogen dissociated during the chemisorption of ethane cannot (at room temperature) migrate to class (B) sites.

Figure 6 confirms the view that the relatively slow exchange reaction of paraffins with deuterium is due to the strong chemisorption of hydrogen on all sites which might otherwise be accessible to the paraffin molecules.[12]

Acknowledgment.—This work was performed under contract with the Office of Naval Research. It is a pleasure also to acknowledge the assistance of Dr. Jean A. Sabatka.

(12) J. Turkevich and H. S. Taylor, THIS JOURNAL, **56**, 2254 (1934).

EVANSTON, ILLINOIS.

[CONTRIBUTION FROM CLIMAX MOLYBDENUM COMPANY OF MICHIGAN]

Preparation and Characterization of a New Crystalline Form of Molybdenum Disulfide

BY RONALD E. BELL AND ROBERT E. HERFERT

RECEIVED FEBRUARY 26, 1957

During an investigation involving preparation of a quantity of synthetic molybdenum disulfide, X-ray techniques were applied to evaluate purity where ordinary wet chemical methods could not be used. The X-ray examinations indicated diffraction patterns differing from the pattern of natural molybdenite. An intensive study by single crystal X-ray techniques revealed that instead of the customary hexagonal molybdenum disulfide structure a hitherto unreported rhombohedral form of the compound had been prepared.

Introduction

The synthesis of molybdenum disulfide by chemical means has been described by a number of early researchers.[1-9] Such various methods of preparation as that proposed by Berzelius,[1] wherein molybdenum trisulfide is decomposed by vacuum heating; or the method of Svanberg and Struve,[2] involving reaction of molybdenum trioxide with hydrogen sulfide gas at red heat; the procedure of heating molybdenum and sulfur in an iron tube as proposed by van Arkel[3]; the procedure of de Schulten,[4] in which molybdenum trioxide, sulfur and potassium carbonate are fused together; the method used by Milbauer,[5] wherein molybdenum dioxide reacted with molten potassium thiocyanate; finally, Lander and Germer deposited molybdenum disulfide coatings from molybdenum carbonyl in atmospheres containing rather critical ratios of hydrogen sulfide and carbon monoxide; are among those listed in the literature.

In these earlier experiments evidence that molybdenum disulfide had been prepared synthetically was based on chemical analysis and, in some cases, also on microscopic examination. Van Arkel[3] reported Debye-Scherrer patterns identical to those obtained with natural molybdenum disulfide for his synthetic product. Other than this, there are no references in which the crystal structure of synthetic molybdenum disulfide has been established by modern crystallographic techniques.

A quantity of molybdenum disulfide of a purity that was not readily obtained by purification of the natural product was required at the authors' laboratory for standardization as to physical, chemical and mechanical properties; therefore, it was proposed to prepare the material by chemical synthesis.

As will be shown, it developed that the material eventually prepared differed from natural molybdenum disulfide in that the crystal structure was not the same.

Experimental

Preparation.—After experimenting with several of the procedures described in the literature and finding them to yield products unsatisfactory for this investigation, the procedure described by de Schulten[4] was applied to the preparation of the subject material. Briefly, this procedure is as follows: four parts by weight of potassium carbonate (reagent grade) are fused with six parts by weight of flowers of sulfur in a 250-ml. covered porcelain crucible at 675°, the reaction being conducted in a gas-fired furnace until evolution of sulfur dioxide is complete. The crucible and contents are removed from the furnace (taking precaution to avoid thermal shock) and allowed to cool. One part of sublimed molybdenum trioxide is added and the crucible is reheated at 900° for 30 minutes. Additional molybdenum trioxide is added in the same manner and the contents of the crucible are reheated at 900° after each addition, until a total of six parts by weight of molybdenum trioxide has been added. The entire mass is solidified, and the excess reagents and impurities are removed from the molybdenum disulfide by prolonged boiling with dilute ammonia, followed by washing with distilled water, boiling for a short time (20 to 30 min.) in dilute hydrochloric acid, and finally, by thorough washing with water, alcohol and ether. The material is then vacuum dried at 75°. The above treatment will not remove the MoO_2 impurity.

Purification.—The chemical reaction involved in de Schulten's method for synthesizing molybdenum disulfide is believed to proceed in two steps

$$2MoO_3 + S \longrightarrow 2MoO_2 + SO_2 \qquad (1)$$

$$MoO_2 + 3S \longrightarrow MoS_2 + SO_2 \qquad (2)$$

(It is assumed that potassium carbonate merely acts as a flux without actually entering into the reaction.)

The procedure just described includes measures which were intended to remove all ammonia and acid-soluble impurities. Upon X-ray diffraction examination of the product, the only detectable impurity not removed by this treatment was molybdenum dioxide.

The presence of molybdenum dioxide as an impurity in the product may be attributed to inhomogeneities in the fusion mass which resulted in local deficiencies of available

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