BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2012—2017 (1967)

Kinetics of the Catalytic Decomposition of Methanol, Formaldehyde and Methyl Formate over a Copper-wire Surface[*1]

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(Received January 26, 1967)

In order to reveal the selective action of nickel and copper in the catalytic decomposition of methanol, kinetic studies of the decomposition of methanol, and methanol-d_1 (CH_3OD), and also of that of formaldehyde and methyl formate, both the assumed intermediates of the methanol decomposition, were undertaken over the temperature range between 100 and 330°C and the pressure range up to 30 mmHg. We also made studies of the exchange reaction of methanol, formaldehyde, or methyl formate with deuterium. The obtained rate equation for the methanol decomposition and the results on the deuterium exchange lead to the following conclusion: the rate is controlled by the unimolecular dehydrogenation of adsorbed methanol, which gives formaldehyde at first and finally hydrogen and carbon monoxide *via* a more stable intermediate, methyl formate. A comparison of activities between copper and nickel was made on the basis of the different behavior of formaldehyde on these catalyst surfaces. The nature of the catalyst surface and of the sites effective for the reaction were also briefly discussed.

In a previous work,[1)] the kinetics of the decomposition of methanol was studied with the nickel-wire catalyst; the reaction was found to be successive, involving the adsorbed formaldehyde as one of the intermediate. The following mechanism was proposed:

$$CH_3OH(g) \rightleftharpoons CH_3O(a)+H(a)$$

$$CH_3O(a)+H(a) \rightarrow CH_2O(a)+H_2(g)$$

$$CH_2O(a) \rightleftharpoons CHO(a)+H(a)$$

$$CHO(a) \rightleftharpoons CO(a)+H(a)$$

$$CO(a) \rightleftharpoons CO(g)$$

$$2H(a) \rightleftharpoons H_2(g)$$

where (a) and (g) denote adsorbed or gaseous species respectively.

The second step, the surface reaction between the adsorbed methoxy radical and the hydrogen atom, was reasonably assumed to be rate-determining.

Since nickel is a typical "d-metal," with an unpaired d-electron in the 3d-orbitals or a d-vacancy in the corresponding electron band, it is interesting to compare its catalytic activity with that of copper, an "s-metal", with filled 3d-orbitals and 4s-electron.

There has, however, been very little work done on the catalytic action of copper in the methanol decomposition, except for those studies[2-4)] which dealt with the production of formaldehyde using copper powder catalysts promoted with CeO_2, ThO_2, and Ag.

In the present work, therefore, kinetic studies were made of the decompositions or dehydrogenations of methanol, methanol-d_1 (CH_3OD), and of the intermediate products formaldehyde and methyl

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[*1] Presented partly at the 17th Meeting of the Catalysis Society of Japan, Tokyo, March, 1966.

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1) I. Yasumori, T. Nakamura and E. Miyazaki, This Bulletin, **40**, 1372 (1967).

2) J. C. Ghosh and J. B. Baski, *Quat. J. Indian Chem. Soc.*, **3**, 415 (1926).

3) J. F. Eversole, U. S. Pat. 2010427 (1933).

4) P. Y. Ivannikov and A. V. Zherko, *J. Appl. Chem. (USSR)*, **6**, 1148 (1933).

formate with the copper wire catalyst; the exchange reactions of methanol, formaldehyde, and methylformate with deuterium were also studied.

On the basis of these results, the validity of the proposed mechanism of the reaction was discussed and the different selective action of copper from that of nickel was considered, with reference to the adsorbed states of the intermediates.

Experimental

Catalyst and Reagents. Copper wire 0.15 mm in diameter, from the Tokyo Wire Co., Ltd., was used as a catalyst. The purity of this wire was confirmed to be 99.9% (by weight) from the spectroscopic analysis.

Six meters of this catalyst wire was prepared in the form of a coil and was oxidized in air of 100 mmHg at 500°C for 1 hr, and then reduced with hydrogen of 70 mmHg at 350°C for 3 hr. These treatments were repeated until a constant activity was attained.

Methanol and methyl formate, of an analytically pure grade, from the Tokyo Kasei Kogyo Co., Ltd., were distilled three times in the presence of metallic magnesium in order to remove a trace of water.

Degassed para-formaldehyde, of a reagent grade, from the Yoneyama Chemical Co., Ltd., was used to produce formaldehyde by heating it about 80°C.

Methanol-d_1 (CH_3OD) was prepared by making use of the exchange reaction between methanol and deuterium; it was verified by a study of the infrared spectra using a Perkin-Elmer 125 spectrometer that the product contained more than 90% of CH_3OD.

Apparatus. The static system described in the previous paper[1] was used for the measurements of the reaction rate, as is shown in Fig. 1, except that a newly-devised manometer system was set in the apparatus in order to carry out the reaction at various initial pressures and to record the pressure change automatically.

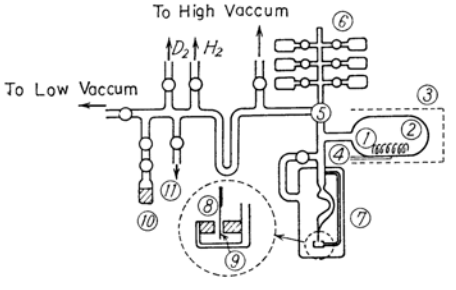

Fig. 1. Apparatus.

1: Catalyst 2: Reaction vessel 3: Electric pile 4: Thermocouple 5: Three way stop-cock 6: Sampling tubes 7: High frequency inductance manometer 8: Ferrite core 9: Aluminum foil (0.1 mm thick) 10: Sample 11: Bourdon manometer

The details of this manometer were previously reported,[5] together with several examples of the measurements; it was found that this instrument can successfully follow rapid changes in the pressure of the reactant, especially at the initial stage of reaction.

The exchange reactions of methanol, formaldehyde, and methyl formate with deuterium were also examined in the static system mentioned above. After the reactant, mixed with equimolar deuterium, was brought into contact with the catalyst for definite time intervals, the products in the gas phase were placed in a mass or an infrared spectrometer for analysis.

Results

Dehydrogenation of Methanol. A typical run of the reaction is shown in Fig. 2; the reaction temperature was 280°C, and the initial pressure of methanol was 21.8 mmHg.

The main products were found to be methyl formate, carbon monoxide, and formaldehyde, the last-named product existing only at the initial stage of the reaction; the concentration of methyl formate showed a maximum throughout the course, while that of carbon monoxide increased gradually with a decrease in the concentration of methyl formate. Hydrogen was also produced, but it was omitted from Fig. 2. This result was quite different from that with nickel, where hydrogen and carbon monoxide were produced from the beginning of the reaction.[1,6]

The initial rate (r_0) of the dehydrogenation on a copper surface was evaluated as an increasing rate of total pressure, since the reaction which gives formaldehyde is followed by the step of dimerization to methyl formate, as may be seen from Fig. 2; this conclusion was confirmed in the later experiments.

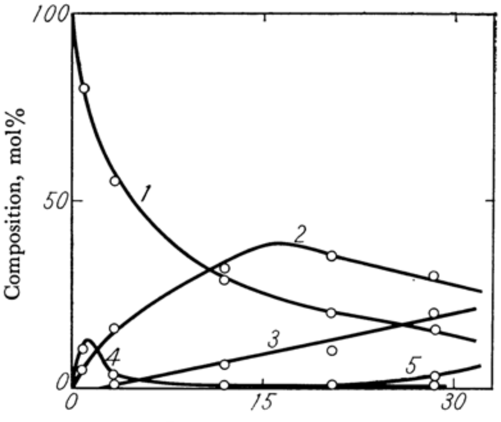

Fig. 2. Change in composition during methanol decomposition over copper-wire catalyst.
Reaction temperature 280°C.
Reaction initial pressure 21.9 mmHg.
1: CH_3OH 2: $HCOOCH_3$ 3: CO 4: H_2CO 5: CO_2

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[5] I. Yasumori, S. Ohno and E. Miyazaki, This Bulletin, **40**, 769 (1967).

[6] E. Miyazaki and I. Yasumori, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1033 (1965).

Thus, the initial rate was well represented by:

$$r_0 = kKP/(1+KP) \qquad (1)$$

where k and K are constants, since the linear relationship between $1/r_0$ and $1/P$ shown in Fig. 3 was obtained.

Since Eq. (1) is similar to that obtained for the decomposition of formaldehyde over a nickel catalyst,¹⁾ it is possible, for the same reaction as has been described previously, to designate by k and K the rate constant of the reaction and the equilibrium constant for the "reactive" adsorption of methanol respectively.

From the dependencies of $\ln k$ and $\ln K$ against $1/T$ (Fig. 4), the true activation energy and the heat of "reactive" adsorption were evaluated as 14.6 and 4.6 kcal/mol respectively; therefore, 10 kcal/mol was obtained for the apparent activation energy.

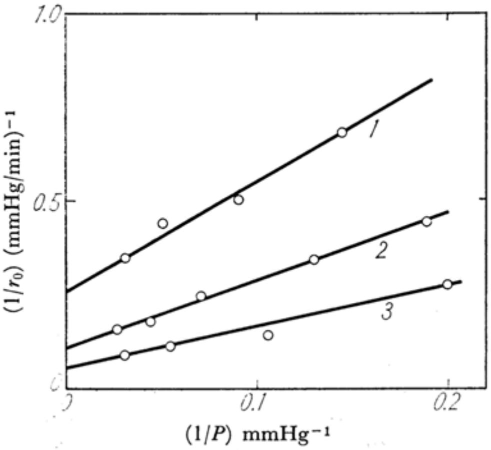

Fig. 3. Linear relationship between $(1/r_0)$ and $(1/P)$ in methanol decomposition over copper-wire catalyst. r_0: Initial rate of the reaction $CH_3OH \rightarrow H_2CO+H_2$
1: 250°C 2: 280°C 3: 310°C

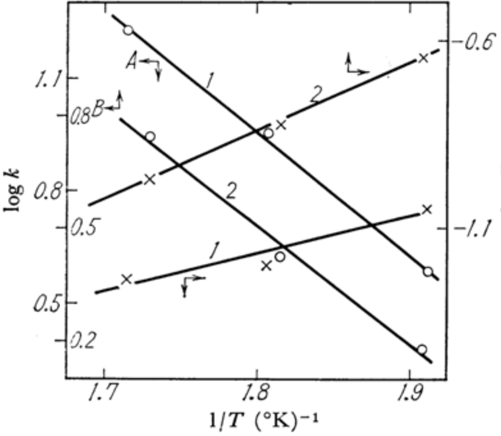

Fig. 4. Temperature dependence of rate constant (k) and adsorption equilibrium constant (K) in dehydrogenation of methanol or methylformate over copper wire catalyst.
1: CH_3OH 2: $HCOOCH_3$

The latter value roughly agrees with the value, 14 kcal/mol, for the alumina-supported copper catalyst obtained by Brihta and Luetic,⁷⁾ but they found only hydrogen and carbon monoxide as products.

The rate equation is, therefore, exactly given as:

$$r_0 = 5.5\times 10^{19}\, g\times \exp(-10000/\boldsymbol{R}T)P/ \{1+1\times 10^{-3}\exp(4600/\boldsymbol{R}T)P\}\ \text{molecules}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}.$$

where g is the roughness factor of the surface and where P is expressed in mmHg.

This expression suggests that the rate-determining step corresponds to the dehydrogenation of adsorbed methanol on the surface, if the reaction proceeds unimolecularly with respect to the adsorbed methanol at the preliminary equilibrium.

Moreover, in order to see in what states the adsorbed methanol exists over the copper surface, the exchange reaction of methanol with deuterium was studied at temperatures both where the decomposition of methanol occurred and where it did not.

It was then found that the copper-wire catalyst is almost inactive for the exchange, even during the course of dehydrogenation, suggesting that methanol is dehydrogenated *via* the state of non-dissociative adsorption.

This result is quite different from that obtained for the nickel catalyst¹⁾; in this case the exchange occurs readily even below the decomposing temperature.

Dehydrogenation of Methanol-d_1 (CH_3OD). The dehydrogenation of methanol-d_1 was studied under the same conditions as in the case of methanol, which are shown in Fig. 2, in order to see the details of methyl formate formation.

Since the dehydrogenation of methanol was supposed to be an unimolecular reaction on the copper surface, it was expected that only hydrogen deuteride atom and light methyl formate ($HCOOCH_3$) were produced through the intramolecular combination of the deuterium atom in the hydroxyl group and the hydrogen atom in the methyl group, and by the following dimerization of the thus-produced formaldehyde, which is adsorbed on the catalyst surface in a non-dissociative form.

In order to eliminate the influence of the successive exchange between the produced methyl formate and HD or D_2, however, the changes in their concentrations should be extrapolated to the beginning of the reaction.

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7) I. Brihta and P. Luetic, *Croat Chem. Acta,* **29**, 419 (1957).

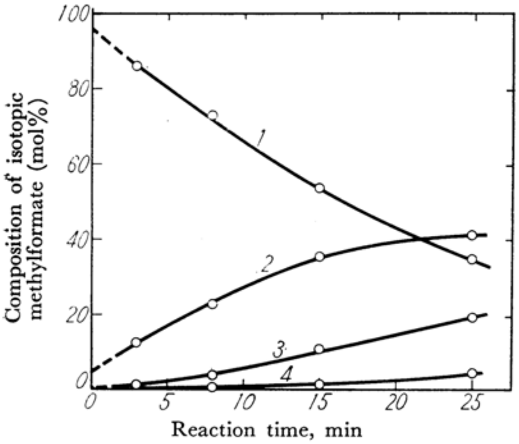

Fig. 5. Change in percentage yields of deuteromethylformates from the decomposition of deuteromethanol (CH_3OD) as a function of reaction time.
1: $C_2O_2H_4$ 2: $C_2O_2H_3D$ 3: $C_2O_2H_2D_2$
4: $C_2O_2HD_3$

Figure 5 shows the composition of methyl formate and its change with time thus obtained. These results, and the fact that only HD was produced at the beginning of the reaction, seem to give support to the mechanism assumed above.

Reaction of Formaldehyde. Methyl formate alone was observed as the product in the reaction of formaldehyde on a copper surface in a moderate temperature range, though the aldehyde decomposed to hydrogen and carbon monoxide over a nickel catalyst. The reaction showed an induction period which, within 1 to 3 min, decreased with an elevation of the temperature. Accordingly, this difference in the formaldehyde reaction was regarded as the main cause of the different selectivities of nickel and copper for the methanol decomposition.

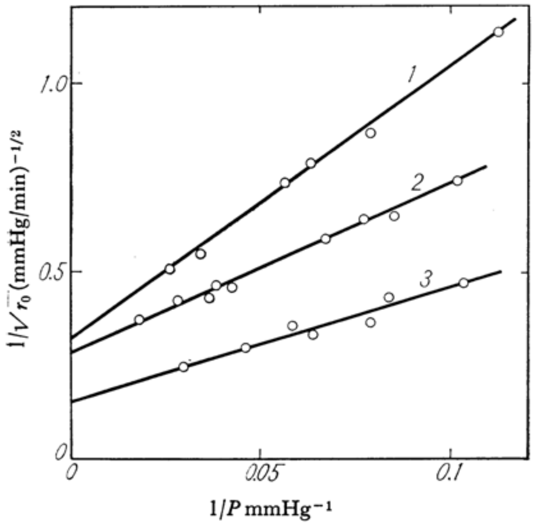

Fig. 6. Linear relationship between $(1/\sqrt{r_0})$ and $(1/P)$ in formaldehyde decomposition over copper wire catalyst.
1: 150°C 2: 163°C 3: 180°C

By inspecting the plots shown in Fig. 6, the form of the initial rate (r_0) was determined to be:

$$r_0=k(KP)^2/(1+KP)^2 \tag{2}$$

from which the dimerization between two adsorbed formaldehyde molecules was supposed to be the rate-determining step.

The true activation energy was 20.6 kcal/mol, which is larger than that in nickel, while the heat of "reactive" adsorption was almost zero.

The exact rate equation for copper was then given as follows:

$$r_0=8\times10^{26}\,g\times\exp(-20600/\boldsymbol{R}T)(0.05P)^2/(1+0.05P)^2\ \text{molecules}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}.$$

Further, the exchange reaction of formaldehyde with deuterium was examined in the temperature range from 80 to 120°C; however, the exchange was not observed even during the reaction, as in the case for the nickel catalyst.[1)]

Decomposition of Methyl Formate and Exchange Reaction of Methyl Formate with Deuterium. The products of methyl formate decomposition on copper were found to be hydrogen and carbon monoxide, plus a small amount (1—2%) of carbon dioxide which increased with the elevation in temperature and with the reaction time.

These products are different from those of a thermal or catalytic decomposition over a silica surface,[8)] where methanol and carbon monoxide are mainly produced.

The $r_0=kKP/(1+KP)$ equation was well adapted to the initial rate of the reaction.

The true activation energy and the heat of adsorption effective for the decomposition were evaluated to be 15.1 and 8.0 kcal/mol respectively from the results shown in Fig. 4.

The exact rate equation is, then, finally given as:

$$r_0=1.5\times10^{17}\,g\times\exp(-7000/\boldsymbol{R}T)P/[1+1.5\times10^{-4}\exp(8000/\boldsymbol{R}T)P]\text{molecules}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}.$$

It was concluded that the surface reaction is also rate-determining and that methyl formate is adsorbed more strongly than methanol on a copper surface, since both the heat and the equilibrium constant of the adsorption were larger than those for methanol under the present experimental conditions.

Therefore, the fact that the concentration of formaldehyde attained a maximum at an early stage of the methanol decomposition and then decreased to an extremely small value in the steady

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8) E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A127**, 314 (1930).

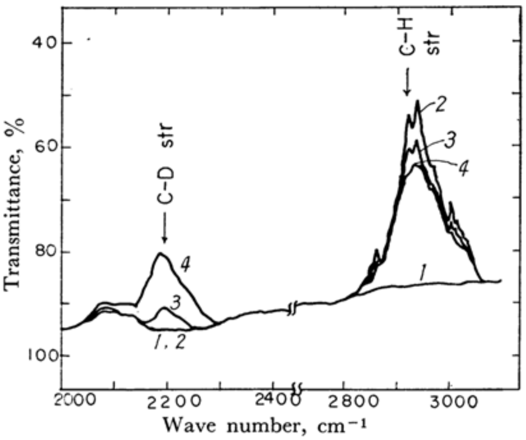


Fig. 7. Infrared spectra of the exchange reaction between methylformate and deuterium over copper wire catalyst.
1. Back ground
2. $HCOOCH_3$
3. $HCOOCH_3 + D_2$ (1 : 1)
After the contact of 16 hr at 195°C
(decomposition was not observed)
4. $HCOOCH_3 + D_2$ (1 : 1)
After 160 min at 248°C
(during decomposition)

state, as is shown in Fig. 2, was explained by the retardation of formaldehyde formation due to a decrease in the number of sites for methanol adsorption, as they were gradually covered with the produced methyl formate.

The exchange reaction with deuterium was examined during the decomposition of methyl formate and at a low temperature where the decomposition was not observed. The results are shown in Fig. 7. The exchanged molecules were identified by the absorption band, 2050—2150 cm^{-1}, due to the C–D stretching vibration; it was confirmed that the reaction occurs where the decomposition proceeds or not.

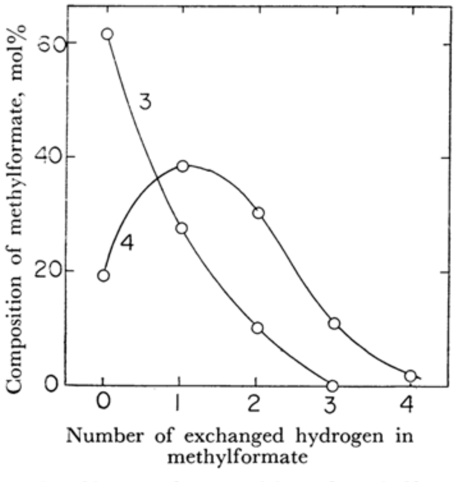


Fig. 8. Change of composition of methylformate as a function of number of exchanged hydrogen in methylformate under the same conditions as in Fig. 7.

In order to see which hydrogen atom, that in the methin or that in the methyl group of methyl formate, is more subject to the exchange, the deuterium distribution in methyl formate was studied by the use of a mass spectrometer; the results are summarized as a function of the exchanged number of hydrogen atoms in Fig. 8.

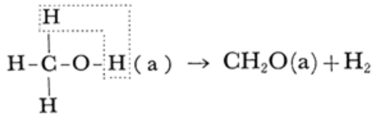
Since the distinction due to the position of hydrogen is not observed from the figure, the exchange seems to occur step by step to give the final form of $DCOOCD_3$. This conclusion is also supported from the change in the composition with the time, as is shown in Fig. 5.

The results obtained above suggest that adsorbed methyl formate exists in a state where the bonds between hydrogen and carbon atoms are somewhat loosened; this loosening is probably induced by the carboxyl group in methyl formate. The details of the adsorbed methyl formate on a copper surface will be reported in a later paper.[9]

Discussion

On the basis of the results given above, the mechanism of methanol reaction over the copper surface may be proposed to be as follows:

$$CH_3OH(g) \rightleftharpoons CH_3OH(a)$$



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H(a) \rightarrow CH_2O(a)+H_2$$

$$CH_2O(a) \rightleftharpoons CH_2O(g)$$

$$2CH_2O(a) \rightleftharpoons HCOOCH_3(a)$$

$$HCOOCH_3(a) \rightleftharpoons HCOOCH_3(g)$$

$$HCOOCH_3(a) \rightleftharpoons 2CO+2H_2$$

The difference in selectivity for the methanol decomposition between the copper and nickel catalysts stems from several factors. At first the "reactive" adsorbed states of methanol differ from each other; on nickel methanol is adsorbed in a dissociative state such as $CH_3O(a)+H(a)$, while it is adsorbed in a non-dissociative form on copper.

Kemball *et al.*[10] also observed, in their study of the exchange reaction of methanol with deuterium, that the reaction occurred on a evaporated film of nickel near room temperature, while not on silver even at about 200°C.

Considering that silver has a catalytic activity for the dehydrogenation of methanol, forming

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9) E. Miyazaki and I. Yasumori, This Bulletin, to be published.

10) J. R. Anderson and C. Kemball, *Trans. Faraday Soc.*, **51**, 966 (1955).

formaldehyde as well as copper, it may be suggested that there is some correlation between the activities of the dehydrogenation and the exchange reaction.

Besides, it is well known that nickel contains 0.6 of an unpaired electron per atom in the d-band; this nickel is responsible for the magnetic properties of the metal, while copper is a s-metal with filled 3d-orbitals and a 4s-electron per atom.

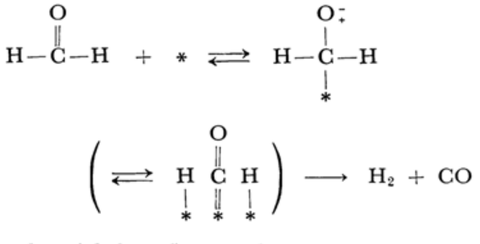
Thus, the comparison of the above experimental results with the electronic configurations of metals lead to the conclusion that an adsorption bond, consisting of electrons from the incomplete d-shell and the adsorbate molecule, is directed and strong enough to dissociate the molecule into several fragments, while the outer s-electron in copper is used for the formation of molecular adsorption, with some loosening of the other bonds in the molecule.

The most important factor in the difference in the selectivity, however, is the role of the produced formaldehyde on the nickel, while it first dimerizes to methyl formate on the copper.

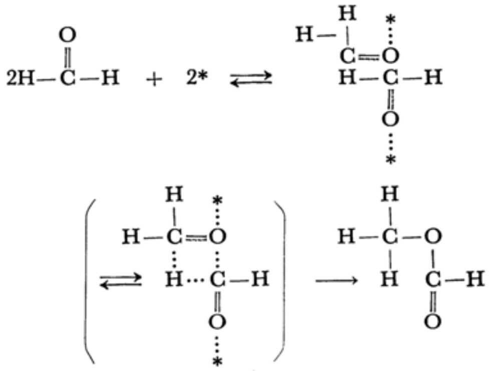
It was found by Culver *et al.*[11] and by Bloyaert *et al.*[12] that the surface potential changes due to the adsorption of carbon monoxide over an evaporated metal film have values between -1.20 and -1.35 V for a nickel and between 0.28 and 0.30 V for a copper.

By combining these data with the infrared spectrum of carbon monoxide on reduced nickel,[13] or with spectroscopic evidence[14] of the molecule coordinated to copper,[12] Culver and Tompkins[15] suggested that the carbon-atom end of carbon monoxide is bound on the nickel surface, while, on the contrary, the oxygen end of the molecule is attached to the copper atom on the surface.

If these chemisorbed states of the carboxyl group can adapted to that of formaldehyde, the reaction of formaldehyde may be said to proceed in such ways as are shown below:



on the nickel surface, and



on the copper surface, where * denotes the site of adsorption and where dotted lines mean transient weak bonds.

On the basis of the kinetic results described above, some considerations can be essayed on the natures of the catalyst surfaces and the adsorbed states.

At first, the active sites for the reaction will be satisfactorilly homogeneous on the surface, since the rate equations are well expressed as of the Langmuir type in every system investigated here.

The previous studies of the methanol adsorption[6] and the hydrogen adsorption on the nickel wire catalyst[16] showed that the highly-sintered nickel surface is homogeneous, but that the portion of adsorptive sites corresponds to only 20% of the total surface area, indicating that the surface sites are divided into several groups which differ from each other in their functions but which are relatively homogeneous within themselves.

This point of view is also supported by Eischens *et al.*[17] who came to a similar conclusion in their infrared spectroscopic study of carbon monoxide adsorbed on palladium from the fact that the number of absorption bands due to the stretching vibrations of adsorbed C–O increased with the surface coverage.

Another piece of information is on the nature of the adsorbed states. The heats of adsorption effective for the reaction calculated from K's are generally smaller than those obtained from the separated measurements of chemisorption. These heats of the reactive adsorption of formaldehyde and methyl formate over the copper surface come in the order of $HCOOCH_3 > H_2CO$; however, reverse order, $HCOOCH_3 < H_2CO$, is, on the contrary, obtained for the true activation energies. This finding is convincing, adsorption bond formed is much stronger than the broken one in the case of methyl formate; therefore, the true activation energy needed to form activated complexes will become smaller.

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[11] R. V. Culver, J. Pritchard and F. C. Tompkins, *Proc. 2nd Intern. Congr. Surface Activity,* **2**, 243 (1957).

[12] F. Boyaert and J. C. P. Mignolet, *J. chim. phys.,* **54**, 53 (1957).

[13] R. P. Eischens, S. A. Francis and W. A. Pliskin, *J. Phys. Chem.,* **60**, 194 (1956).

[14] R. P. Eischens, W. A. Pliskin and S. A. Francis, *J. Chem. Phys.,* **22**, 1786 (1954).

[15] R. V. Culver and F. C. Tompkins, *Advances in Catalysis,* **11**, 107 (1959).

[16] E. Miyazaki and I. Yasumori, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.),* **85**, 415 (1964).

[17] R. P. Eischens and W. A. Pliskin, *Advances in Catalysis,* **10**, 14 (1958).