Study on Zinc Oxide-Chromium Oxide Catalyst. II. Variation of Catalytic Activity for Methanol Decomposition with Addition of Chromia and Structural Dependence of Activity

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Introduction

Zinc oxide-chromium oxide, used as a catalyst for the methanol synthesis, has been the object of intense studies made by a number of investigators since about thirty years ago. Nevertheless, most of the works have been made only on the catalytic activity of the substance in the methanol synthesis as well as in the methanol decomposition, and a knowledge sufficient for understanding the activity in relation to the structure of the catalyst is still lacking.

The present study has been made in an attempt to see as correct and comprehensive a picture of such catalysts as possible, and deals with the electrical conductivity, the surface area, the crystal structure, and the excess oxygen content, of catalysts of different chromia contents, along with their catalytic activity for methanol decomposition. The results of the activity may be explained, to some extent, from the structural point of view.

Experimental Procedure

Catalyst Preparation.—Two series of catalysts were prepared. The catalysts of the one series, each denoted by catalyst I, were produced by the impregnation of commercial zinc oxide powder (c. p.) in chromium nitrate solutions of varied concentrations and the catalysts of the other series, each denoted by catalyst P, were by the co-precipitation of the hydroxides of zinc and chromium from solutions of zinc and chromium nitrates of different relative concentrations with aqueous ammonia. The powder of catalyst thus formed was heated at 400°C for a few hours and then pressed into a bar of 8×8 mm. square. The bar was sintered at 600°C in air for two hours and then allowed to cool to room temperature. Part of the bar was crushed into granules of 1-2 mm. diameter, to be used for the determination of activity in methanol decomposition and the surface area.

Catalytic Activity for Methanol Decomposition.—The experimental method consisted of passing methanol vapour at a constant rate of 1.98 m. mol./min. through a bed of granular catalyst in a vertical glass tube heated to temperatures from 350° to 430°C in an electric furnace. The apparatus was similar to the one described by J. R. Huffman et al.[1], but was different from it in that the constant rate was maintained, as performal by M. R. Fenske et al.[2], by immersing the methanol reservoir in a water bath at a constant temperature.

A bed of catalyst (1 g.) was reduced at 450°C in a current of hydrogen for six hours, and then methanol vapour was passed through the bed at the reaction temperature. About two hours were required for the catalyst to establish the stationary activity, and measurements were commenced thereafter. The products, gaseous and liquid, were collected and their amounts were determined. The gaseous product was analyzed, as is usually done, for carbon dioxide, carbon monoxide, and hydrogen, and the liquid product was analyzed both for methyl formate by saponification and for formaldehyde by the iodine method.

Electrical Conductivity.—As described in a previous paper[3], electrical conductivity was measured according to the method of R. H. Griffith et al.[4], by using a cube of catalyst (8×8×8 mm.) as a sample. Measurements were made first in vacuo both after the oxidation of the catalyst in oxygen at 450°C and after the reduction in hydrogen at 450°C, and second in an atmosphere of hydrogen after the measurement on the reduced catalyst.

Crystal Structure.—Information on crystal structure was furnished by the Debye-Scherrer's X-ray diagram obtained by using chromium as an anode. It was supplemented by the electron diffraction pattern of powdered catalyst.

Surface Area.—Surface area was determined from the nitrogen adsorption data plotted according to the BET theory.

Quantity of Excess Oxygen in Catalyst.—The excess oxygen content was determined according to the procedure by S. W. Weller[5]. One mole of iodine liberated from an aqueous solution of potassium iodide by the addition of a quantity of catalyst was estimated to be equivalent to 0.5 mol. excess oxygen in the catalyst. A powder of catalyst under 100 mesh was used for the determination.

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[1] J. R. Huffman and B. F. Dodge, *Ind. Eng. Chem.*, 21, 1056 (1929).

[2] M. R. Fenske and P. K. Frolich, ibid., 21, 1052 (1929)

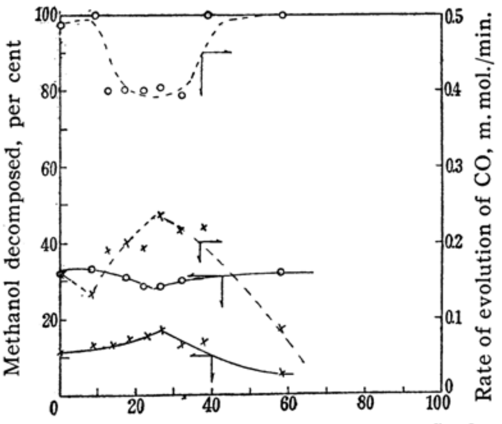
[3] H. Uchida and Y. Ogino, This Bulletin, 29, 174 (1956).

[4] R. H. Grifith, P. R. Chapman et al., *Disc. Faraday Soc.*, 8, 258 (1950).

[5] S. W. Weller and S. F. Voltz, *J. Am. Chem. Soc.* 76, 4695 (1954).

Results

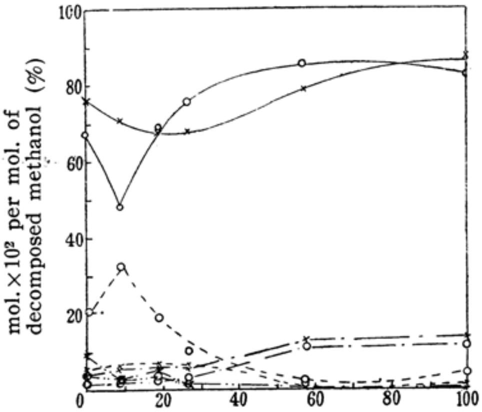
Catalytic Activity for Methanol Decomposition.—Among the results of the measurement of activities of catalysts in methanol decomposition at temperatures from 350° to 430°C, the results for catalysts I at 350° and 400°C are shown in Fig. 1 and Fig. 2. In Fig. 1, the total decomposition ratio of methanol ($CH_3OH_{decomp.}/CH_3OH_{introd.}$) and the rate of evolution of carbon monoxide (mole CO/min.) are illustrated by the full and dotted lines respectively, as functions of catalyst composition. In Fig. 2, the composition of decomposition product is plotted also as such. The results for catalysts P are presented in similar manner in Figs. 3 and 4.



Composition of catalyst, mol. per cent Cr_2O_3

Fig. 1. Total decomposition ratio (full line) and rate of evolution of carbon monoxide (dotted line) as a function of $ZnO-Cr_2O_3$ composition of catalysts I.

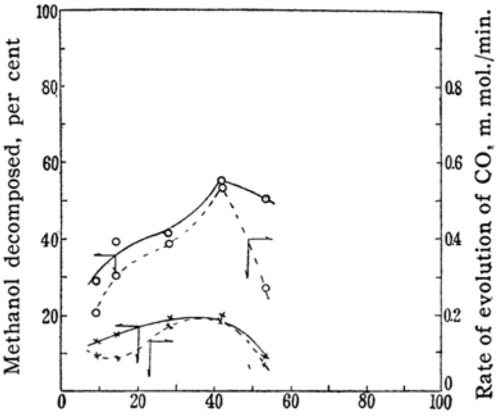
—×—, --×--, at 350°C. —○—, --○--, at 400°C



Composition of catalyst, mol. per cent Cr_2O_3

Fig. 2. Products of methanol decomposition as a function of $ZnO-Cr_2O_3$ composition of catalysts I.

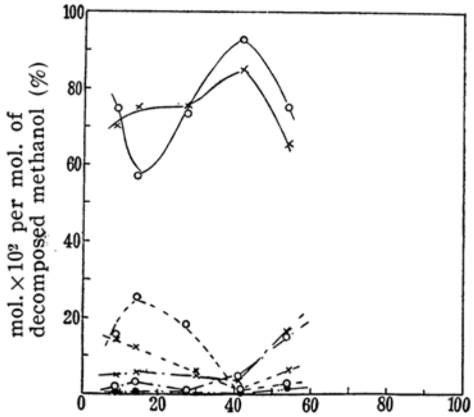
—○— CO, at 350°C. —×— CO, at 400°C
--○-- $HCOOCH_3$, at 350°C
--×-- 〃 , at 400°C
—..—○..— HCHO, at 350°C
—..×—..— 〃 , at 400°C
—.○—.— CO_2, at 350°C
—.×—.— 〃 , at 400°C



Composition of catalyst, mol. per cent Cr_2O_3

Fig. 3. Total decomposition ratio (full line) and rate of evolution of carbon monoxide (dotted line) as a function of $ZnO-Cr_2O_3$ composition of catalysts P.

—×—, --×--, at 350°C. —○—, --○--, at 400°C



Composition of catalyst, mol. per cent Cr_2O_3

Fig. 4. Products of methanol decomposition as a function of $ZnO-Cr_2O_3$ composition of catalysts P.

—○— CO, at 350°C. —×— CO, at 400°C
--○-- $HCOOCH_3$, at 350°C
--○-- , at 400°C
—..●—.. HCHO, at 350°C
, at 400°C
—.—○—. CO_2, at 350°C
—.—×—. , at 400°C

It can be seen from Figs. 1 and 3 that at 350°C a catalyst containing, for example, 26 mol.% chromia gives the highest values of the total decomposition ratio and the rate of evolution of carbon monoxide, whereas at

400°C it gives rather lower values. Fig. 5 is a detailed representation of the data on the decomposition. This figure shows that the rates increase logarithmically with reciprocal absolute temperature but differently depending on the compositions of the catalysts. Therefore, catalytic activity can not be evaluated correctly unless measurements are made over a wide range of temperature.

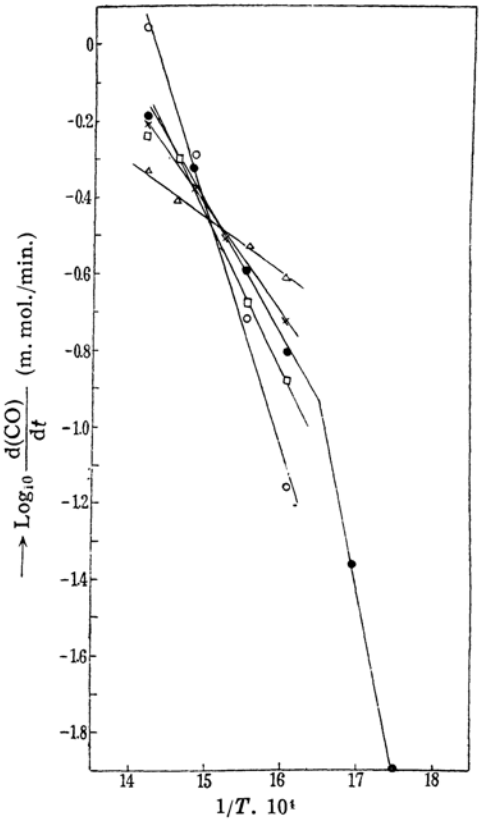


Fig. 5. Temperature dependence of rate of evolution of carbon monoxide.

—●— , *zinc oxide.*

—○— , catalyst I containing 58.6 mol.% chromia within.

—△— , 〃 26.3 mol.%

—□— , 〃 9.5 mol.%

—×— , 〃 14.3 mol.%

There is a good similarity in tendency between the full line and the dotted line, both in Fig. 1 and in Fig. 3, except for the case of a catalyst containing 10 mol.% chromia. This catalyst yielded a greater amount of methyl formate particularly at a low temperature of 350°C (refer to Figs. 2 and 4)[*1], but gave a lower rate of evolution of carbon monoxide despite the greater decomposition ratio.

On the basis of H. Dohse's view that the methanol decomposition follows a zeroth order reaction, the apparent activation energy of methanol decomposition by the catalysts I was given by the slope of the straight line in Fig. 5. The activation energy thus determined is lowest at a chromia content of 26 mol.%, whereas it rises with decreasing chromia content on the one side and also with increasing chromia on the other side (refer to Fig. 10 also). The more active a catalyst is at lower temperatures, the smaller is the activation energy, whereas the more active a catalyst is at a higher temperature, the greater is the activation energy.

H. Dohse[7] described that the plot of log v vs. $1/T$ for zinc oxide has a bend. Such a bend appears also at 330°C on the line constructed from the present data of experiments, and is of particular interest in view of the fact that a bend, as will be described later, appears also on the plot of electrical conductivity vs. $1/T$ for zinc oxide at the same temperature. The bend in the conductivity curve, however, shifts, with the increasing chromia content, towards so low a temperature that the corresponding bend in the activity curve can scarcely be determined accurately (refer to Fig. 7).

A comparison of the activation energy of the catalysts I with that of the catalysts P indicates that within the range of chromia content of up to 30 mol.% the energy for the latter is greater than that for the former and beyond this content the situation is reversed (refer to Fig. 10).

Electrical Conductivity.—The results of the measurements of electrical conductivity on evacuated catalysts at 350°C, which were made both after the oxidation and after the reduction of catalysts at 450°C, are shown as functions of catalyst composition in Fig. 6[*2]. The electrical conductivity of the oxidized, evacuated catalysts is the higher for the increasing chromia contents, whereas that of the reduced, evacuated catalysts is the lower for the increasing chromia content. In Fig. 6, the conductivity curve for oxidized, evacuated catalysts intersects that for reduced evacuated catalysts, at a certain chromia content, which is 26 mol.% for the catalysts I, and 13 mol.% for the catalysts P.

The catalyst has naturally the conductivity centres of two types, the one is the zinc

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[*1] This may perhaps have a close relation to the highly selective catalyst that was used in the methanol synthesis by G. Natta[6] and which contained 11 mol. % of chromia.

6) G. Natta, "Catalysis (edited by P.H. Emmett)", Rheinhold Publishing Corporation, (1955), III, P. 349.

7) H. Dohse, *Z. Physik. Chem.*, **B** 8, 159 (1930).

[*2] The conductivity of the oxidized catalysts in oxygen atmosphere differed little from that of the oxidized, evacuated ones.

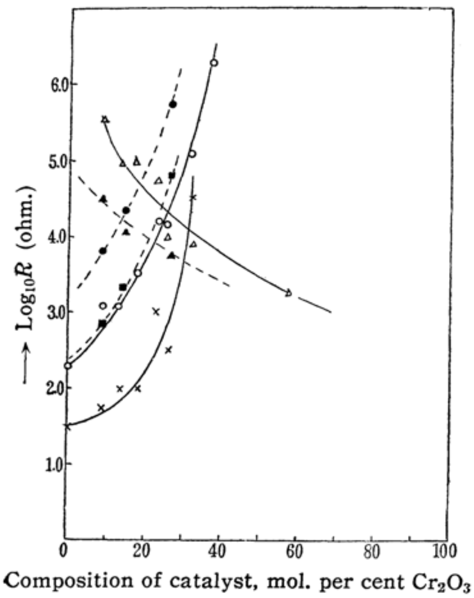

Fig. 6. Electrical conductivity of catalysts I (full line) and catalysts P (dotted line) at 350°C as a function of ZnO–Cr_2O_3 composition.

×, ■, in hydrogen after reduction
○, ●, in vacuo after reduction
△, ▲, in vacuo after oxidation

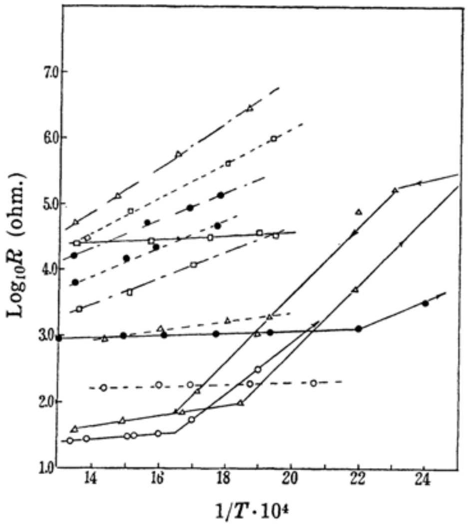

Fig. 7. Temperature dependence of electrical conductivity of catalysts I in hydrogen (full line), in vacuo after reduction (dotted line), and in vacuo after oxidation (dotted and dashed line).

○, zinc oxide. △, catalyst with 9.5 mol. % Cr_2O_3. ●, , , , 23.3 mol. %. □, , , , 33.2 mol.%

atoms (n-type) due to zinc oxide and the other the excess oxygen atoms (p-type) due to chromia. This fact implies that the n-type semi-conductivity becomes predominant in the catalysts of reduced state whereas the p-type becomes so in the catalysts of oxidized state, and that the greater amount of chromia favour the production of a larger number of p-type centres.

Logarithms of electrical resistivity determined on the catalysts in vacuo both after the oxidation and after the reduction of catalysts at 450°C, and those of catalysts in the hydrogen atmosphere after the reduction at the same temperature, are plotted against reciprocal temperatures in Fig. 7[*3]. As for the catalysts I in the hydrogen atmosphere, the plots for every catalyst form a pair of straight lines intersecting at a certain temperature that shifts to lower values with increasing contents. The change of the electrical conductivity with the lowering temperature was not reversible by the subsequent raise of temperature, and showed a pronounced drift.

The slope of the straight line in the high temperature range should give the activation energy of electrical conductivity in this range[*4]. The energy thus determined for catalysts in hydrogen depends on the chromia content of catalysts. Within the range of low chromia content (less than about 26 mol.%), the energy rises slightly with the increase of chromia content and soon reaches a maximum at about 10 mol.% chromia and thereafter takes a downward course to a minimum at 26 mol.% chromia, and this decrease is followed by a rapid rise with the further increasing chromia content (refer to Fig. 10).

In contrast, the activation energy of conductivity for catalysts evacuated after their reduction rises monotonously with increasing chromia content, whereas the energy for the catalysts evacuated after their oxidation persists almost unaffected by the increase of chromia content.

Catalyst Structure Revealed by Debye-Scherrer's X-ray Diagram and Electron Diffraction Pattern.—The catalysts I and catalysts P gave Debye-Scherr's X-ray diagrams that did not show any line corresponding to Cr_2O_3, even though the catalysts were heated at 600°C for two hours and their chromia contents were as high as 59%, but showed the lines corresponding to zinc oxide.

The diffraction lines for zinc oxide, however, become weaker with increasing chromia content. Besides these lines, the lines cor-

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[*3] The electrical conductivity of catalysts P at temperatures below 300°C was not determined.

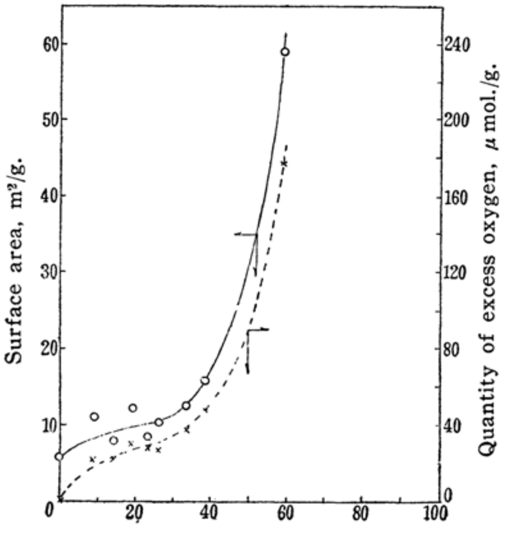
[*4] Considering the performance of catalysts at the practical working temperature, the energy in the low temperature range is of minor significance.

responding to neither zinc oxide nor Cr_2O_3 but to $ZnCr_2O_4$ spinel were observed. The lines due to the spinel appeared even at so small a chromia content as of 9.5 mol.% and their number increased with the chromia content increasing up to 25–30 mol.%, but above this content the lines became gradually diffused till it was difficult to distinguish the lines.

The electron diffraction patterns for catalysts I and catalyst P reveal also the lines due to the spinel. The number of these lines is far greater than the number of the diffraction lines in the X-ray diffraction diagram. The electron diffraction lines remained sharp while the chromia content increased even up to the value where the X-ray diffraction lines became rather diffused.

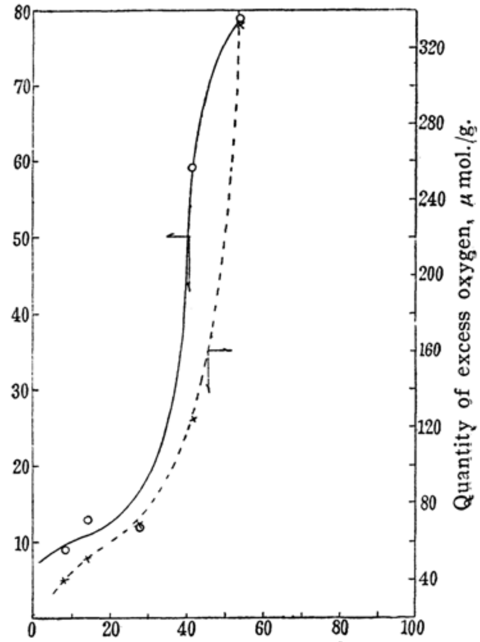
The results described above reveal that the catalyst comprises the oxides of zinc and chromium and the spinel of zinc chromite presumably produced by the reaction $ZnO + Cr_2O_3 \rightarrow ZnCr_2O_4$, and that the spinel in the catalyst of high chromia content exists as crystallites too small to be detected by the X-ray analysis. Accordingly, the quantity of chromia in excess of the proper amount for combination with zinc oxide seems to prevent the growth of the crystallites.

Surface Area and Quantity of Excess Oxygen in Catalyst.—The surface area of and the quantity of excess oxygen in 1 g. of catalysts are illustrated by the full and the dotted lines respectively, as functions of chromia content, in Fig. 8 for catalysts I, and in Fig. 9 for catalysts P. As is seen in these figures, every curve has a sigmoid shape and rises with increasing chromia content. The initial part (over very low chromia contents), an almost rectilinear line, shows a rather rapid rise, the middle part a very dull rise, and the last part a rise becoming very sharp. The last part begins when the chromia content attains to 35 mol.% for catalysts I, and 30 mol.% for catalysts P.



Composition of catalyst, mol. per cent Cr_2O_3

Fig. 8. Surface area (full line) of and quantity of excess oxygen (dotted line) in 1 g. of catalysts I as a function of $ZnO-Cr_2O_3$ composition.



Composition of catalyst, mol. per cent Cr_2O_3

Fig. 9. Surface area (full line) of and quantity of excess oxygen (dotted line) in 1 g. of catalysts P as a function of $ZnO-Cr_2O_3$ composition.

The results described above may bring out the following picture of the surface structure of catalysts. As revealed by the trend of the surface area change, the size of the larger particles having composed granules of zinc oxide changes a little even though the chromia content attained to 30 mol.%, and any further addition of chromia results in the abrupt creation of numerous fine particles as to catalysts I, whereas it results in the sudden reduction of the particle size as to catalysts P.

For the reason that excess oxygen can exist only in the presence of the chromia which fails to combine with zinc oxide, the steep rise of the excess oxygen curve in the range of high chromia content indicates that the quantity of uncombined chromia is increasing rapidly on the surface of the catalyst. On the other hand, the deviation of the curve from the expected rectilinear line with increasing chromia content is suggestive of the formation of crystallites between the oxides of zinc and chromium[*5]. From the results seen in the diffraction patterns, the crystallite may be the one of zinc chromite spinel. The highest concentration of the spinel crystallites in the surface, therefore, is to be found with catalysts whose excess oxygen content deviates most greatly from the quantity expressed by the expected rectilinear line[*6].

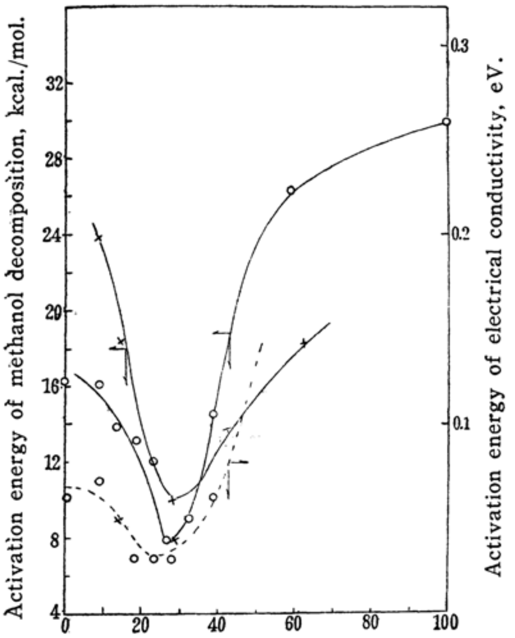


Fig. 10. Variation of activation energies for methanol decomposition (full line) and electrical conductivity (dotted line) with catalyst compositions.
○, catalysts I. ×, catalysts P.

Discussion

Methanol Decomposition.—By assuming that the rate of methanol decomposition follows the zeroth order reaction given by

$$v=Ae^{-E/kT} \quad (1)$$

where v is the rate per unit surface area of the catalyst, the logarithms of frequency factor ($\log A$) are plotted against activation energy (E) in Fig. 11 for catalysts I and catalysts P. The lines for the two kinds of catalysts are straight and approximately identical. The linear relation between $\log A$ and E has already been described by E. Cremer[8], for the rate of methanol decomposition with neodium oxides, and by G–M. Schwab[9], for the rate of the decomposition of formic acid with alloy catalysts, and some others.

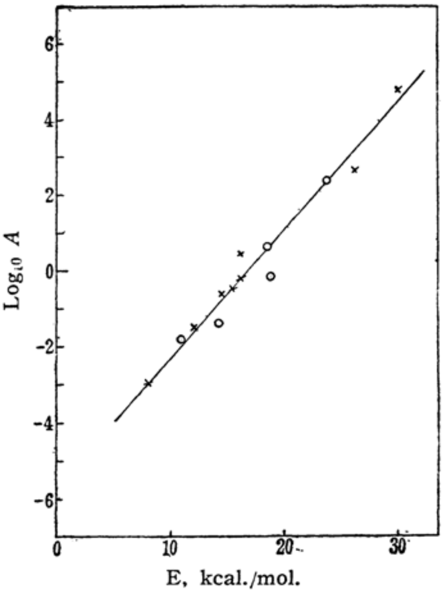


Fig. 11. Plot of logarithm of frequency factor in the rate of evolution of carbon monoxide vs. activation energy.
—×—, catalysts I. —○—, catalysts P.

The straight line can be represented by an equation,

$$A=ae^{\alpha E} \quad (2)$$

where $\log a$ is the intercept on the ordinate and α is the slope of the line. This equation is explained by assuming that active centres with high activation energy in the catalyst surface are more frequent than the ones with low activation energy[9].

The combination of Eq. (2) with Eq. (1) gives

$$v=a\cdot e^{\alpha E}\cdot e^{-E/kT} \quad (3)$$

When v is expressed in the number of moles of carbon monoxide evolved per unit surface (cm^2) per second the substitution of the values of a and α obtained from Fig. 10 in Eq. (3) results in

$$v=1.24\times10^{-7}\cdot e^{0.81E}\cdot e^{-E/kT} \quad (4)$$

Eq. (4) indicates that the rate at a certain temperature, so far as the rate per unit

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[*5] The slow increase within the range of very low chromia content can not readily be explained. The increase is probably due to the condition that chromia is too dispersed to build up the spinel crystallite, though it is combined with zinc oxide.

[*6] A greater amount of the crystallites may be produced in 1 g. of the catalyst by the further addition of chromia, but since the amount considered is based on the unit surface area it becomes rather less owing to the steep rise of surface area.

[8] E. Cremer, *Z. Elektrochem.*, 53, 269 (1949).

[9] G-M. Schwab, *Disc. Faraday Soc.*, 8, 166 (1950).

surface area is considered, is determined solely by the activation energy inherent to a catalyst, but not by any other factors.

Catalytic Activity and Electrical Conductivity.—At first sight, one may be inclined to expect the relation of the activation energy of methanol decomposition to the concentration of either the *n*-type or the *p*-type conductivity centres in the catalyst. Namely, the concentration of *n*-type conductivity centres need be only adequately low to permit electrons to transfer more readily from methanol to catalyst, and the transfer thus taking place causes the catalyst to adsorb methanol and cosequently to decompose methanol with less activation energy, if the rate of adsorption determines the rate of decomposition of methanol. However, there is a minimum of the activation energy at a catalyst (26 mol.% chromia) of *n*-type semiconductor in I series, whereas at a catalyst (30 mol.% chromia) of *p*-type semi-conductor in P series[*7]. Thus, no direct relation of the activation energy of methanol decomposition to the types of semiconductor can easily be found at all[*8].

When both the activation energy of methanol decomposition and the activation energy of electrical conductivity are plotted as functions of the composition of catalysts I (Fig. 10), the line for the activation energy of methanol decomposition runs parallel to the line for the activation energy of electrical conductivity. Moreover, both the bend in the plot $\log R$ (in hydrogen) and the bend in the plot of $\log v$ vs. $1/T$ for zinc oxide appear at the same temperature (compare Fig. 5 with Fig. 7). A couple of these results serve as a favourable evidence for corroborating the rather direct relation between the activation energies of methanol decomposition and electrical conductivity.

In a previous paper3) it is stated that the decrease of electrical conductivity of zinc oxide in hydrogen with the rise of temperature in the low temperature range was caused by the adsorption of hydrogen on zinc atom-pairs whereas the increase of electrical conductivity in the high temperature range was due to the adsorption on oxygen atoms. This fact in connection with the evidence just described for the relation between activation energies of methanol decomposition and electrical conductivity may lead us to expect that the rate of adsorption of a reactant (methanol or something intermediate in the decomposition) on oxygen atoms (or the electron transfer between the reactant and oxygen atoms) is determining the rate of the methanol decomposition.

Promoting Action of Chromia.—In the methanol decomposition the increase in exponential terms of the rate equation (1) is always compensated by the decrease in the frequency term. According to a recent paper by E. Cremer10), this compensation effect may be expected at multicomponent catalysts of the same type, if different kinds of active centres act simultaneously as sites of the catalytic reaction and if the proportions of these different active centres (involving different energies) are shifted by changes in its composition. An illustration is given by E. Cremer on a reaction that takes place on two kinds (1 and 2) of active centres involving the activation energies E_1 and E_2 and frequency factor terms A_1 and A_2, respectively. In this case the overall rate constant k (or the rate v of a zeroth order reaction) becomes

$$k=A_1\exp(-E_1/kT)+A_2\exp(-E_2/kT),$$

and the Arrhenius plots of k for the greater values of A_2, the values of E_1, E_2 and A_1 being kept at the same, give the straight lines of decreasing slope, i. e. the decreasing activation energy, and of a common intersection point, provided that A_1 is greater than A_2 and E_1 greater than E_2.

A comparison of Fig. 10 with Fig. 8 or 9 indicates that the greater the spinel concentration in the catalyst surface the smaller is the activation energy of methanol decomposition. The fact may be explained as follows from E. Cremer's point of view. In the surface of the catalysts within the range of chromia content up to 26 per cent, zinc oxide and zinc chromite (or the oxygen atoms in zinc oxide and zinc chromite) are the two kinds (1 and 2) of the active centres for the methanol decomposition, while chromia and zinc chromite are such in the surface of the catalyst of higher chromia content. Accordingly, the catalyst with the greater concentration of zinc chromite spinel in the surface can give the smaller activation for the methanol decomposition than both the zinc oxide and chromia alone, if the activation energy of the spinel is assumed to be smaller than that of zinc oxide and of chromia.

No direct relation between the extent of the surface area and the activity for meth-

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[*7] According to D. J. Bevan et al. (*J. Chem. Soc.*, 1948, 1729), zinc chromite is a *p*-type semi-conductor.

[*8] The influence of the concentration of *n*-type semiconductor on the catalytic activity can not completely be denied, particularly at low temperatures where the adsorption of a reactant, as will be described later, takes place on zinc atom pairs.

10) E. Cremer, "Advances in Catalysis", VII((1955), p. 85.

anol decomposition can be found. The activity at, for example, 350°C rose at first with the slow increase of surface area, but thereafter fell off despite the rapid further increase of surface area (compare Fig. 8 with Fig. 10). This result can be explained from the fact that while the surface area increases slowly the activation energy decreases, but once the surface area has begun to increase rapidly the energy turns to increase steeply. The greater amount of the chromia disintegrates the crystallites of the spinel into so extremely fine ones that it may cause the steep increase of surface area and also cover the surface to such an extent that the activation energy approaches a value as high as 30 kcal./mol. for chromia alone.

The favourable effect of chromia is thus to increase the specific activity of catalyst surface rather than to provide and stabilize the larger accessible area. This is quite contrary to G. Natta's statement[6] that the activation energy of methanol synthesis is independent of the chromia content and the promoting action of chromia is solely due to its hindering effect upon the recrystallization of zinc oxide. No decisive conclusion can as yet be made between these two different promoting actions revealed in the synthesis and in the decomposition.

Summary

From the results on the rates of methanol decomposition by the catalysts of different zinc oxide-chromium oxide compositions the rate (v) of evolution of carbon monoxide per unit surface area of catalyst has appeared to be represented by the following equation

$$v = ae^{\alpha E} \cdot e^{-E/kT}$$

where a and α are constants applicable throughout the two series of catalysts produced by different methods. The activation energy (E) of the methanol decomposition attains to a minimum value when the catalyst has a certain chromia content. It is directly related with the activation energy of electrical conductivity of the catalyst in hydrogen at high temperature but neither with the concentration of n-type conductivity centres nor with that of p-type conductivity centres. At such temperatures, the adsorption of hydrogen on the oxygen atoms in the surface was considered to participate in the electrical conductivity.

Moreover, the results on determinations of the surface area and the excess oxygen content, together with the information about the structure obtained from diffraction patterns, reveal that there is a similarity in tendency between the increase of concentration of zinc chromite spinels in the catalyst surface and the decrease of activation energy of the decomposition. This relation can be explained from the view of E. Cremer on the compensation effect.

The quantity of chromia added in excess of the proper amount for combination with zinc oxide causes both the surface area and the activation energy to increase towards those of chromia alone.

The addition of chromia has therefore a considerable influence upon the activation energy of methanol decomposition, which is quite contrary to what G. Natta described on the methanol synthesis.

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