into account. Results of preliminary calculations show that even a very small surface elasticity ($\gg A/8\pi h_0^2$) is usually sufficient to make the surfaces behave as rigid. When surface elasticity is completely absent (no surfactant present), drainage and growth of fluctuations are greatly accelerated and bursting occurs starting at much thicker films. More definite calculations, including surface elasticity and diffusion of surfactant, are now made in a cooperation between our Laboratory and the Unilever Research Laboratory at Vlaardingen, Netherlands (Dr. M. van den Tempel, *et al.*).

Combined Action of Metal and Semiconductor Catalysts[1]

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Contribution from the Institute of Physical Chemistry, University of Munich, Munich, Germany. *Received November 27, 1967*

Abstract: The slow oxidation of methanol vapor in an oxygen stream has been investigated by chromatographic methods. Zinc oxide and silver are both catalysts of the reaction and differ in specificity. A combination of both catalyst powders shows a surprisingly superior action. The result is compared with other similar observations and is interpreted on the basis of boundary layer theory. The idea of electron transfer from the metal into the semiconductor is confirmed by conductivity measurements.

In previous work it has been shown that the activity of a metal catalyst can be modified by supporting the catalyst on a semiconductor.[2-4] More intensive effects have been achieved by spreading a semiconductor catalyst on a metal carrier.[5-7] From this point of view, zinc oxide as catalyst has been used for the oxidation of methanol in the temperature range between 100 and 400°.

The first experiments were made with zinc powder which, as is well known, consists of zinc particles covered by zinc oxide. A dynamic reactor was used as described by Ettre and Brenner[8] and by Menold.[9] The products of the reaction were analyzed on a Perkin-Elmer gas chromatograph, Model 116 E. To achieve high resolution, the method of switching between three different columns was applied (column R, polypropylene glycol on Celite; column JoCe, silica gel; and column I, molecular sieve, 5 Å from Perkin-Elmer).

In these experiments no difference could be observed between the zinc powder described and pure zinc oxide. Therefore we sought to determine whether silver, already proved as an active carrier, would exert an effect. A mixture was prepared from fine silver powder and fine zinc oxide powder, pressed into pellets, and powdered once more. This mixture, designated below as "Ag·ZnO," was placed in a boat in the reactor at a methanol partial pressure of 100 torr in an air stream. In the temperature range between 100 and 150° an explosion was observed, although, over the single catalysts zinc oxide and silver, oxidation starts only at temperatures as high as 250°.

The lower explosion limit of a methanol–air mixture is 6% by volume of methanol. Therefore, further experiments were carried out with a methanol partial pressure of 38 torr corresponding to 5.3 vol %. It is admitted that now, in view of the smaller yield, reaction products formed in small amounts can no longer be analyzed.

The results of the measurements are represented by Figures 1–4. The partial pressures of the reaction products CO_2, H_2O, H_2, and CO have been plotted as a function of the reaction temperature for the following catalysts: ZnO, 0.8 g of ZnO powder; Ag, 0.8 g of Ag powder; Ag·ZnO, equal amounts by weight mixed as above, total weight 0.8 g; Ag + ZnO, 0.4 g of ZnO powder and 0.4 g of Ag powder in two separate boats. Interchange of the relative positions of silver and zinc oxide in the gas stream gave identical results, indicating full longitudinal diffusion mixing.

The following results can be seen in the figures. Carbon dioxide is formed by all the catalysts used, water vapor is formed in all cases except with pure zinc oxide, hydrogen is not formed by silver and by the mixed catalyst, and carbon monoxide is formed only by zinc oxide and only intermediately. It appears that the presence of silver generally suppresses the formation of carbon monoxide; as for hydrogen as a product, silver alone does not give it and it even suppresses its final occurrence with the mixed catalyst.

The most striking fact, however, is that the mixed catalyst gives an extremely high yield in water vapor and carbon dioxide as low as the temperature range between 130 and 200°, in contradistinction to the single catalysts which are not active below 250° and even higher than Ag + ZnO which shows a synergistic effect in Figures 1 and 2.

Methyl formate, formaldehyde, and formic acid could not be traced in any case, probably for the reason

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[1] Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 13, 1967.

[2] G.-M. Schwab, *Angew. Chem.*, **73**, 399 (1961).

[3] G.-M. Schwab, J. Block, and D. Schultze, *ibid.*, **71**, 101 (1959).

[4] G.-M. Schwab and G. Mutzbauer, *Z. Physik. Chem.* (Frankfurt), **32**, 367 (1962).

[5] G.-M. Schwab and R. Siegert, *ibid.*, **50**, 191 (1966).

[6] G.-M. Schwab and H. Derleth, *ibid.*, **53**, 1 (1967).

[7] G.-M. Schwab, F. Steinbach, H. Noller, and M. Venugopalan, *Z. Naturforsch.*, **19a**, 445 (1964); *Nature*, **193**, 774 (1962); see also F. Steinbach, *Angew. Chem.*, **79**, 1019 (1967); *Nature*, **193**, 774 (1962).

[8] L. S. Ettre and N. Brenner, *J. Chromatog.*, **3**, 524 (1960).

[9] R. Menold, *Chem.-Ing. Tech.*, **32**, 801 (1960).

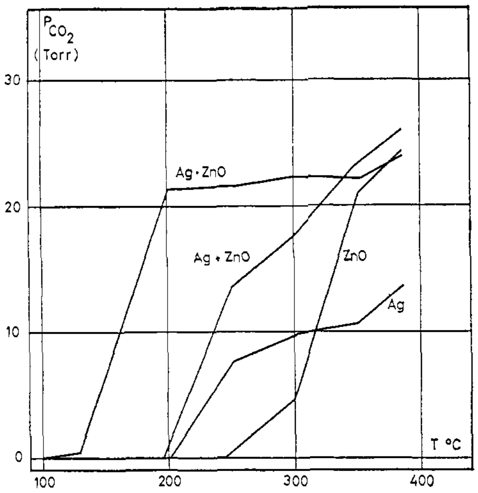

Figure 1. Partial pressure of carbon dioxide as a function of temperature.

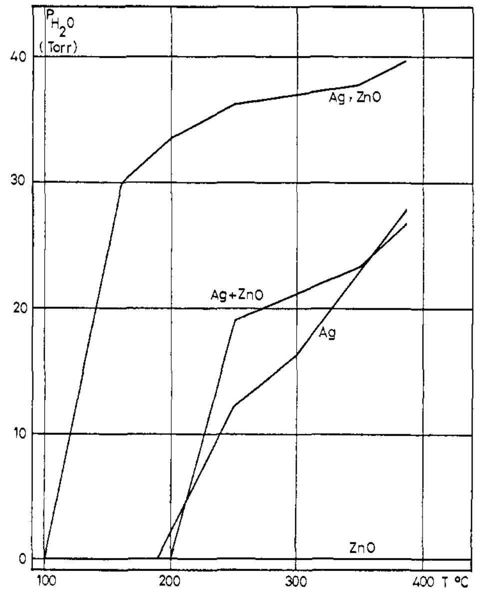

Figure 2. Partial pressure of water vapor as a function of temperature.

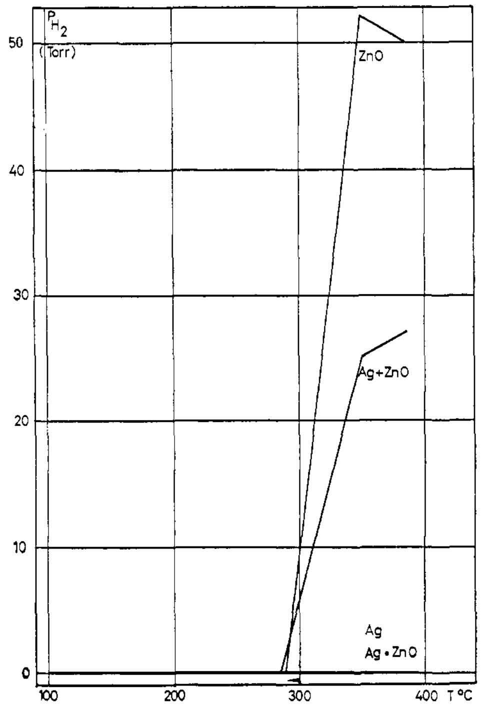

Figure 3. Partial pressure of hydrogen as a function of temperature.

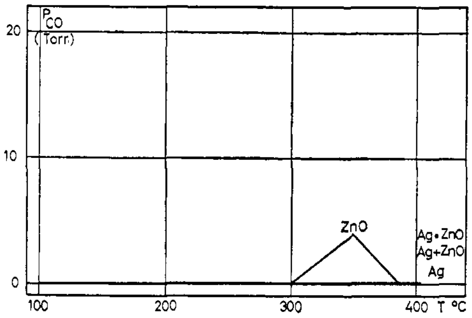

Figure 4. Partial pressure of carbon monoxide as a function of temperature.

mentioned above. It may, however, also be that these products do not occur at all because the disappearing part of the methanol is first completely decomposed and the products CO and H_2 are oxidized giving CO_2 and H_2O. This would explain the high yield of these products and the absence of CO and H_2 over the mixed catalyst.

The oxidation of methanol over zinc oxide has been thoroughly examined by Steinbach, *et al.*[7] Kinetic measurements with and without illumination of a zinc oxide layer, combined with similar experiments on CO oxidation, lead to a mechanism which, in papers still in press, is further supported by observations on zinc oxide layers supported by different evaporated metal films. It is in agreement with all the different observations.

Oxygen is adsorbed on electron-conducting zinc oxide and forms adsorption centers for methanol. Methanol molecules are added by formation of hydrogen bridges (Figure 5). After that methanol is decomposed giving hydrogen and formaldehyde (Figure 5). In the air stream hydrogen is oxidized at the silver catalyst giving water which desorbs, and formaldehyde is once more adsorbed through hydrogen bridges and is decomposed giving carbon monoxide and hydrogen in the same way.

The atomic distances H–H in the organic molecules and O–Zn are of comparable order of magnitude (Figure 6), so that hydrogen bridges are possible. Eischens and Pliskin[10] have proved the existence of such bridges in zinc oxide loaded with hydrogen.

In the case of the metal semiconductor mixed catalyst Ag·ZnO, silver enhances the formation of adsorption centers for methanol.[7] Electrons are emitted from the metal carrier into the catalyst, and these electrons favor the chemisorption of oxygen. This can be represented by the band model in Figure 7. The magnitude $E_c - E_F$ determines the electron concentration n_e in the boundary layer.

$$n_e = N_C e^{-(E_C - E_F)/kT}$$

The distance $E_c - E_F$ in the boundary layer is apparently diminished by the presence of the metal carrier.

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(10) R. P. Eischens, W. A. Pliskin, and M. J. D. Low, *J. Catalysis*, **1**, 180 (1962).

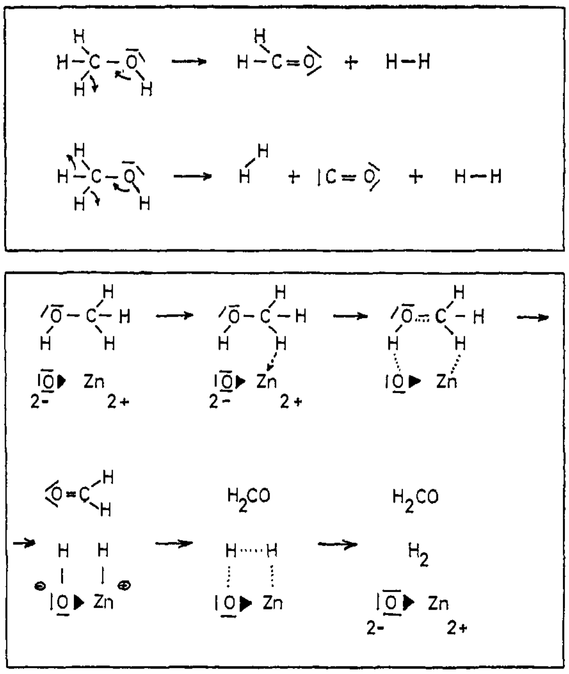

Figure 5. Reaction mechanism of methanol dehydrogenation.

Steinbach[7] has investigated the oxidation of carbon monoxide over a zinc oxide layer with and without a silver film as support in the dark and under ultraviolet irradiation. He found with zinc oxide in the dark an activation energy of 20.6 kcal/mole and with zinc oxide on a silver support 9.0 kcal/mole. Here again the catalytic action of zinc oxide has been enhanced by the silver support. Illumination increases this last value again to the original amount of 20.6 kcal/mole. The reason is considered to be that on irradiation electrons are raised from the valence band and migrate to the positive potential of silver. The remaining positive holes are filled by electrons from the conduction band. Thus the electron concentration in the boundary layer, first increased by the silver support, decreases once more.

In these cases the catalytic promotor effect in a mixed catalyst is traced back to an electron exchange between support and catalyst. However, it cannot be excluded from the experiments hitherto made and is even suggested by a certain amount of synergism in Ag + ZnO (Figures 1 and 2) that the catalyst is essentially bifunctional. It might be that zinc oxide exerts a methanol chemisorption as described above, whereas silver chemisorbs oxygen in the form of atoms[11] and that these atoms (or another intermediate unstable species) diffuse through the contact zone from one component of the catalyst to the other one. Further experiments are planned to discriminate these two possibilities.

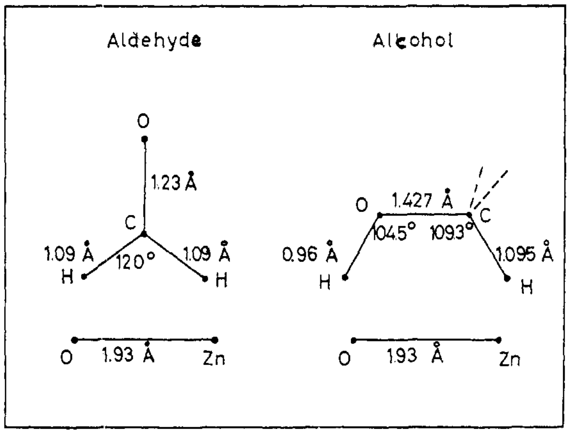

Figure 6. Atomic distances.

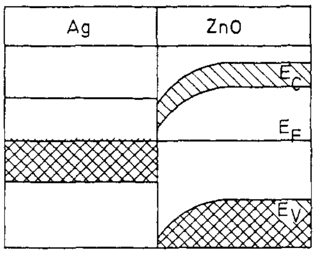

Figure 7. Band model of mixed catalyst.

In the meantime, Mr. Kritikos in this laboratory has confirmed the idea of electron transfer from silver into zinc oxide by conductivity. He could show that addition of a few per cent of silver to a compressed pellet of zinc oxide or another n-type conducting oxide increases the conductivity in the temperature range between 300 and 700°. This effect can be explained by the electron transfer mentioned; it is, however, to be expected from the higher conductivity of silver. On the other side, however, in a p-type conducting material like NiO or Cu_2O, the same percentage of metallic silver does decrease the conductivity in the same range. This proves that electrons actually have gone over from the metal into the semiconductor where they have recombined with positive holes, thus diminishing the conductivity in spite of the higher conductivity of silver itself.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for the support of this work.

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(11) M. D. Thomas, I. N. Vlodavets, *et al.*, cited by J. K. Dixon and J. E. Longfield in "Catalysis," Vol. VII, H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1960.