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Simultaneous Adsorption of Hydrogen and Carbon Monoxide on Zinc Oxide

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The simultaneous adsorption of carbon monoxide and hydrogen on zinc oxide was investigated at −46°, 0°, and 25°C, using gas mixtures of composition 1 CO:1 H_2 and 1 CO:2 H_2. At 0° and 25°C there was mutual enhancement in the adsorption of gases while at −46°C the adsorption was the same as with the pure gases. It is suggested that in mixed adsorption two processes take place, namely, the creation of sites by one gas for the adsorption of the other and the formation of complexes of the type =CHOH in the adsorbed phase.

INTRODUCTION

In previous communications (*1, 2, 3, 4*) studies of simultaneous adsorption of hydrogen and carbon monoxide on cobalt Fischer-Tropsch catalysts have been reported. In almost every case, the adsorption of each gas has been found to be enhanced in the presence of the other. These results have led to interesting speculations relative to the primary catalytic processes involved in the Fischer-Tropsch synthesis of hydrocarbons.

Carbon monoxide and hydrogen react in an apparently different manner over oxide catalysts, notably zinc oxide, leading in the end to the production of methanol under conditions of high pressure and temperature. In view of this apparent difference between the over-all reactions on transition metals and oxides it was considered worthwhile to investigate how the two gases influence each other's adsorption on zinc oxide.

EXPERIMENTAL

Preparation of the Adsorbent Sample

Pure zinc oxalate prepared by adding zinc acetate solution to hot ammonium oxalate solution (analar reagents, calculated quantities) was decomposed completely to zinc oxide by heating it under vacuum at 350° to 400°C for several hours. The zinc oxide thus prepared was slightly yellow in color and 13.2 g of it was used directly for the adsorption measurements.

Preparation and Purification of the Gases

Hydrogen. Electrolytic hydrogen was further purified by passing it in series over (i) hot reduced copper (wire form), (ii) an active platinum catalyst at room temperature to remove traces of oxygen, (iii) freshly regenerated granular anhydrous magnesium perchlorate (drier), and finally (iv) through a silica gel trap cooled in liquid nitrogen to remove the remaining traces of condensable gases and vapors.

Carbon monoxide. This was prepared by dropwise addition of formic acid to glacial phosphoric acid at 170°C, and was purified by passing the gas successively through a

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column of caustic potash pellets, hot reduced copper, caustic potash pellets again, and finally freshly regenerated granular magnesium perchlorate.

Helium. Compressed helium of over 99.5% certified purity was passed over hot copper, anhydrous magnesium perchlorate, and finally through a trap containing activated carbon cooled in liquid nitrogen.

All the gases after purification were collected over mercury and transferred to globes attached to the adsorption apparatus. The gases could be drawn in regulated quantities as and when required into the gas burette and catalyst chamber from the globes.

Measurement of Adsorption

The adsorption measurements were carried out in a conventional volumetric apparatus (Fig. 1) fitted with an all glass electromagnetic gas circulating pump of the type described by Porter, Bardwell, and Lind (*5*) to circulate the gas mixture through the catalyst tube and with a thermal conductivity cell (Katharometer, Cambridge Instrument Co., Ltd., London) for gas analysis. The measurements were made under constant volume conditions. The dead space was determined using helium.

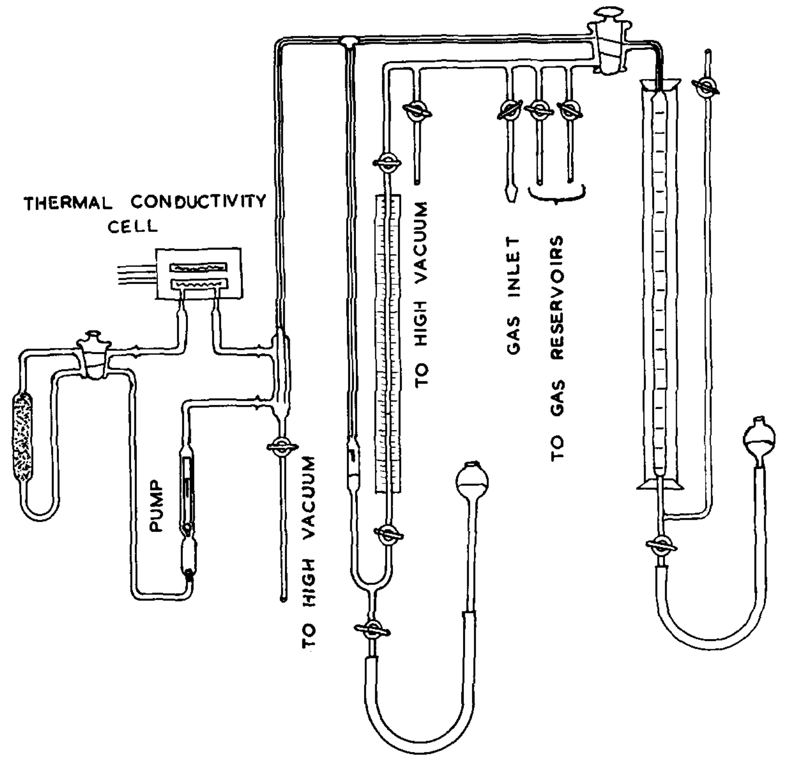


FIG. 1. Adsorption apparatus.

Test for Reaction

The following procedure was adopted to determine the maximum temperature up to which adsorption from the gas mixtures could be studied without the complication of any appreciable reaction occurring between them, such as would lead to the formation of water, carbon dioxide, hydrocarbons, etc. The test was conducted *in situ* in the adsorption apparatus itself.

An equimolar CO-H_2 mixture was circulated over the catalyst for 24 hours at the test temperature, and the residual gas withdrawn very slowly through a trap cooled in liquid nitrogen into a gas sampling receiver where it was collected over mercury. The trap with its attached manometer and receiver is shown in Fig. 2.

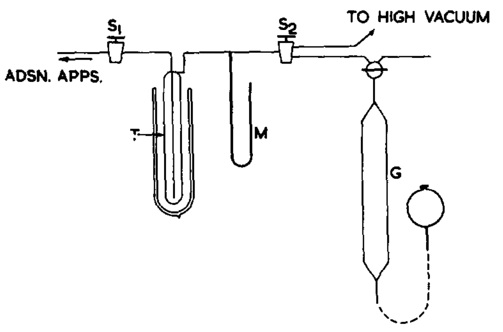


FIG. 2. Setup for testing for reaction.

After most of the gas had thus been withdrawn and collected, the trap was pumped down to 10^{-5} mm with stopcock S_1 closed, and then isolated by closing the other stopcock also. It was then allowed to warm up to room temperature by removing the liquid nitrogen bath. Formation of condensable products showed up by a rise in pressure.

To test for uncondensed products, the gas collected in the receiver was analyzed by gas chromatography, using a molecular sieve column in a Perkin-Elmer Vapor Fractometer.

While tests at temperatures up to 35°C showed no trace of reaction products of any kind in the system, a little hydrocarbon (methane) was found in tests performed above this temperature. The adsorption measurements were therefore carried out at temperatures up to 25° to keep the maximum by a safe margin below that required for appreciable reaction occurrence.

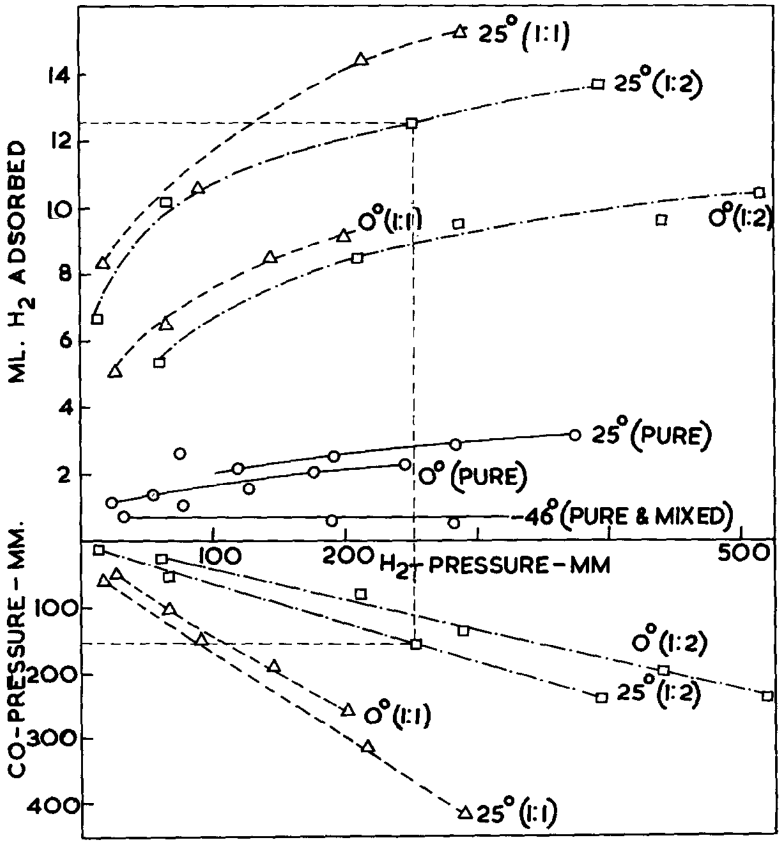


FIG. 3. Adsorption isotherms of hydrogen from mixtures of carbon monoxide and hydrogen.

Degassing Schedule

The following procedure was adopted uniformly for degassing the catalyst before the adsorption runs both with pure gases and mixtures. The catalyst was initially evacuated for 2 hours at the temperature of the adsorption run, after which the temperature was gradually raised to 400°C, and the evacuation continued at the latter temperature for a further 4 hours. A two-stage mercury diffusion pump was used and the steady vacuum obtained was always better than 10^{-5} mm Hg.

RESULTS

Adsorption of hydrogen and carbon

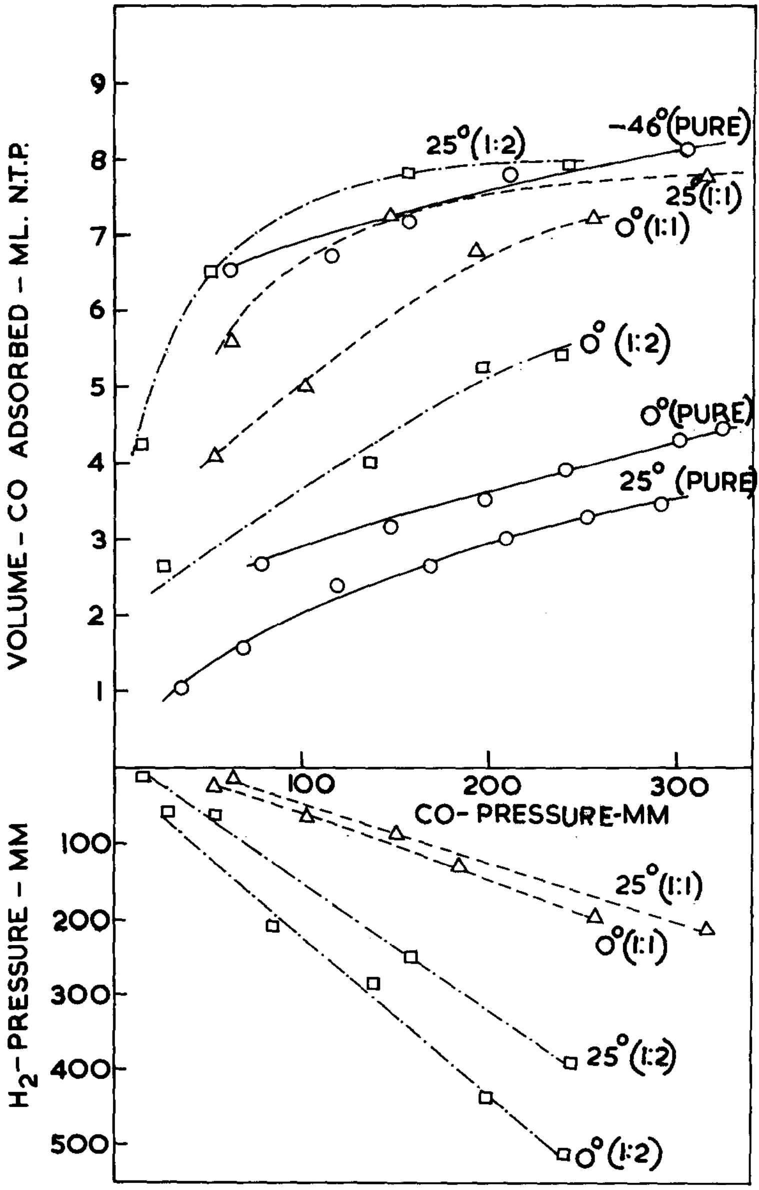


FIG.4.

FIG. 4. Adsorption isotherm of carbon monoxide from mixtures of carbon monoxide and hydrogen.

monoxide individually from the pure gases as well as from the 1 CO:1 H_2 and 1 CO: 2 H_2 mixtures was determined at —46°, 0°, and 25°C. The isotherms obtained are shown in Figs. 3 and 4. In these figures and in the following discussion the mixture designations 1 CO:1 H_2 and 1 CO:2 H_2 refer to the approximate *initial* compositions of the gas mixtures admitted to the system. The equilibrium compositions attained eventually in contact with the catalyst can be gauged from the plots of the individual partial pressures given in the lower parts of Figs. 3 and 4 where the equilibrium pressure of one of the gases is plotted against the corresponding partial pressures of the other gas. For example in Fig. 3 when 12.5 cc of hydrogen is adsorbed from a 1 CO:2 H_2 mixture at 25°C, the partial pressures of hydrogen and carbon monoxide in the gas phase are 252.5 mm and 155 mm respectively.

With the pure gas isotherms, it is found that with increase of temperature the adsorption of hydrogen increases while that of carbon monoxide decreases. From the mixtures, however, the adsorption of each gas increases with the temperature.

At the lowest temperature studied, namely —46°C, the adsorption of each gas from either mixture almost coincided with the corresponding pure gas isotherm. The mixed gas isotherm for this temperature could not therefore be shown separately in Figs. 3 and 4. At the higher temperatures, 0° and 25°C, however, the adsorption isotherms of either gas from the mixtures run above the corresponding pure gas isotherms. In other words, at these temperatures, the adsorption of each gas is enhanced in the presence of the other, the observed enhancement being greater at 25° than at 0°C.

The composition and growth of the adsorbed phase can be followed from the plots of hydrogen and carbon monoxide adsorbed simultaneously from the mixtures presented in Fig. 5.

At 0°C the over-all composition of the adsorbed phase depends on the composition of the gas phase, being richer in carbon monoxide when formed from the 1 CO:1 H_2 mixture. The dependence of the substrate composition on that of the gas phase was confirmed independently as follows. The catalyst was exposed to 1 CO:1 H_2 mixture at 0°C. When the adsorption became steady the total gas pressure was about 30 cm and the individual adsorptions fell almost exactly on the 1 CO:1 H_2 isotherm for 0° in Fig. 3. When sufficient hydrogen was admitted to change the composition of the

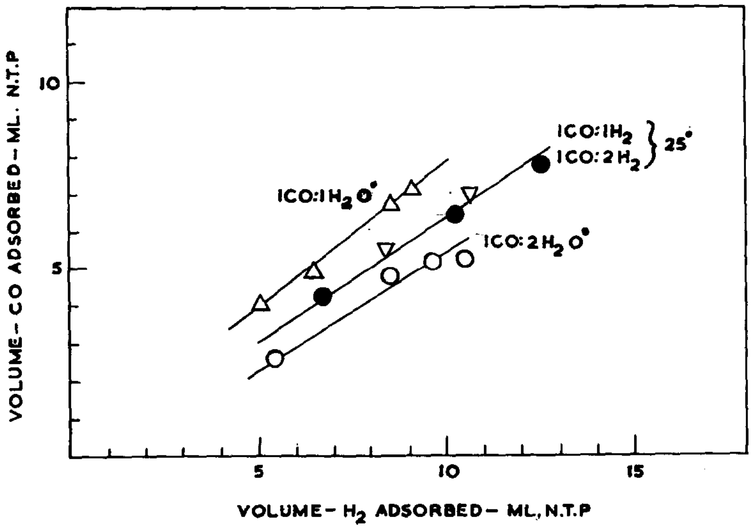


FIG. 5. Substrate composition.

gas to 1 CO:2 H_2, hydrogen was found to be taken up rapidly until the substrate composition corresponded to that obtained from 1 CO:2 H_2 mixture at the same total pressure.

At 25°C however, the composition of the adsorbed phase was found to be independent of the gas composition. A similar observation recorded in the case of CO–H_2 adsorption on cobalt Fischer-Tropsch catalysts (*2*) was considered to indicate strongly the formation of adsorbed $\equiv$COH complexes on the surface.

Discussion

Hydrogen chemisorption at temperatures below 50°C does not produce any change in the conductivity of zinc oxide, while carbon monoxide chemisorption decreases the conductivity (*6*). The absence of any change in the conductivity of zinc oxide on hydrogen chemisorption rules out the possibility of the participation of the loosely bound electrons of the "defect" solid in bond formation. The bond formed must be weaker than a covalent bond since at these temperatures rapid H_2–D_2 exchange can take place (*7*). To explain these observations it has been postulated, in conformity with the suggestion of Volkenstein (*8*) and of Volkenstein and Roginskii (*9*), that the adsorbed hydrogen atoms are attached to the defect sites by one-electron bonds forming a complex where the electron from the hydrogen remains localized and therefore does not contribute to the alteration of the conductivity.

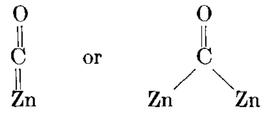
When carbon monoxide is adsorbed at these temperatures the electrons loosely bound to the surface zinc atoms are either donated to or shared with the CO molecule in the formation of the chemisorption bond, thus causing a decrease in the conductivity of zinc oxide.

In the mixed adsorption of carbon monoxide and hydrogen, mutual enhancement of adsorption can result due to either the creation of additional sites for the adsorption of one gas by the presence of the other or due to the formation of complexes between the two gases or due to the simultaneous operation of both mechanisms.

The chemisorption of hydrogen which shares its electron to form the Zn–H bond creates additional donor levels and reduces the surface charge barrier. This creates a situation favorable for carbon monoxide adsorption. Carbon monoxide on the other hand by sharing the electrons of the zinc oxide facilitates the formation of Zn–H bonds where the hydrogen donates its electron. Thus they will mutually help each other's chemisorption. However, since chemisorption is an equilibrium process the actual amount of gases adsorbed will depend on the partial pressure of the gases.

When carbon monoxide and hydrogen are chemisorbed simultaneously on zinc oxide, the interaction of the electron clouds of the chemisorbed species is likely to be indistinguishable from complex formation. The initial substrate composition is proportional to the gas phase composition at 0°C, but independent of it at 25°C. At both temperatures, when the substrate is growing, additional amounts of carbon monoxide and hydrogen are taken up in a constant ratio of nearly 1:1 (Fig. 5). This result and the fact that at 0°C hydrogen is adsorbed to a greater extent from the mixture poorer in hydrogen suggest that complex formation plays a more predominant role, at least during the later stages of the mixed chemisorption at these temperatures. It is more so at 25°C than at 0°C.

The formation of $=$CHOH and —CH_2OH complexes wherein more than one H atom is attached to each chemisorbed CO and hence to each site, can lead to enhancement of hydrogen chemisorption. The transformation of the configuration of the adsorbed complex from



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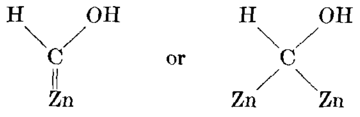
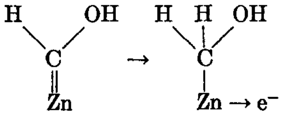


will lead to a decrease of the anionic charge with consequent decrease of the negativity of the surface dipole ($Zn\text{–}CO^-$) owing to the attachment of covalent hydrogen and hydroxyl in place of the $=O$. This would reduce the energy barrier against the extraction of electrons from the solid and thus facilitate further CO chemisorption. With the further hydrogenation of the complex to $-CH_2OH$ the effect becomes even more marked and straightforward, because with the reduction of the double bond to a single bond between zinc and carbon



the surplus electron which is released from the double bond should flow back into the solid and become available immediately for further CO chemisorption and complex formation.

The over-all results show that at 0°C the two processes of additional site creation and complex formation take place at more or less comparable rates. The increase in importance of one mechanism over the other with a 25° rise in temperature would mean that the formation of complexes involves a higher energy of activation than the creation of sites.

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