

Adsorption Measurement during the Decomposition of Methanol on a Methanol Synthesis Catalyst

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The adsorption as well as the rate during the course of the methanol decomposition on a methanol synthesis catalyst with three components have been investigated. The amounts of adsorption of both hydrogen and carbon monoxide or any complex formed from them during the decomposition were greater than those from the mixture of $2\text{H}_2:1\text{CO}$. No decrease in the ambient pressure of hydrogen was observed at the sudden removal of methanol from the gas phase during the course of the decomposition reaction by means of a dry ice trap. The rate-determining step of the decomposition of methanol is suggested to be the process of dissociation of the adsorbed methanol into the adsorbed intermediate and hydrogen. The initial amount of adsorption of methanol during the reaction was the saturation value expected from v_m in the BET equation. The empirical zero order kinetics is explained on the basis of the saturated adsorption of methanol on the catalyst surface.

INTRODUCTION

Extensive studies (1-6) have been carried out on the methanol decomposition reaction over methanol synthesis catalyst and, in most cases, the rate of the reaction has been expressed by an equation

$$r = k$$

where k is a rate constant. It is generally admitted that the reaction is of the zeroth order when the catalyst surface is fully covered by the reactant or the reaction intermediate, and it would be proved if the adsorption were measured during the methanol decomposition reaction. In a previous paper (7), the authors suggested that the rate-determining step of the methanol synthesis reaction is a process of the Eley-Rideal type—hydrogenation of an adsorbed surface complex. The reverse reaction of this step would therefore be suggested to be the rate-determining step of the methanol decomposition reaction. In order to confirm these surmises, the adsorption as well as the reaction rate have been measured during the decomposition of methanol.

EXPERIMENTAL

The apparatus employed is a closed circulating system schematically illustrated in the previous paper (7). Known amounts of methanol were introduced into the system and the decomposition followed, the pressure and the composition of circulating gas being measured at suitable time intervals. The composition of the circulating gas mixture comprised of methanol, hydrogen, carbon monoxide, and carbon dioxide was determined by gas chromatography after removing methanol by means of a trap. The amount of methanol in the gas phase was estimated from the decrease in the total pressure by trapping and the volume of the system. The amounts of gases adsorbed on the catalyst surface were obtained from the material balances either of hydrogen or of carbon. These were expressed as either hydrogen or carbon monoxide. Due allowance was made for analytical samples removed from the reacting system.

The catalyst employed had the composition $\text{Zn}:\text{Cr}:\text{Cu} = 1.0:0.49:0.16$, and was

reduced for 280 hr at 280°C under atmospheric pressure in a hydrogen stream saturated with methanol vapor at room temperature. Before each run the catalyst was evacuated for 3 hr at 400°C and thus the experimental results were quite reproducible.

RESULTS

Typical results of the decomposition of methanol are shown in Figs. 1 and 2, where

the amounts of the adsorption of hydrogen and carbon monoxide from 2H₂:1CO premixed gases at their corresponding partial pressures in the decomposition, the amounts of their adsorption being obtained from the pressure-adsorption curves for 2H₂:1CO premixed gases. The amounts of adsorption of hydrogen and carbon monoxide represented by H₂(a) and CO(a), respectively, include the adsorbed complex formed from hydrogen and carbon monoxide as well as

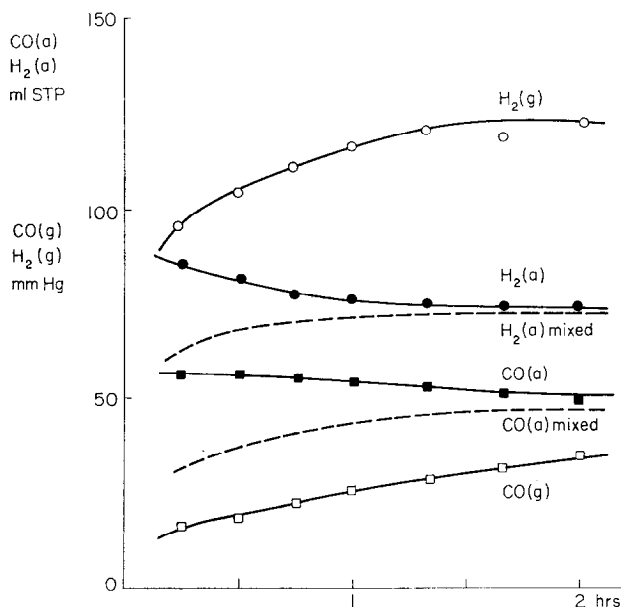


FIG. 1. Adsorption measurements during the methanol decomposition reaction at 250°C (catalyst 19.7 g).

the amounts of catalyst employed were 19.7 and 1.46 g, respectively. In the case shown in Fig. 1, the amount of methanol in the gas phase became less than 2% of the total gas in a few minutes. In the case shown in Fig. 2, where a much smaller amount of the catalyst was employed, the amounts of methanol in the gas phase could be followed with time. As the decomposition proceeded, the partial pressure of methanol decreased with time, and those of hydrogen and carbon monoxide increased, while the adsorption of hydrogen and carbon monoxide decreased as shown in Figs. 1 and 2. The dotted lines in the figures represent

the uncombined hydrogen and carbon monoxide. The amounts of the adsorption of both hydrogen and carbon monoxide during the decomposition reaction were always greater than those in the adsorption from 2H₂:1CO premixed gases.

When methanol in the circulating gas was abruptly removed from the system by cooling a trap with dry ice, the ambient pressure of hydrogen did not decrease as shown in Fig. 3. A symbol \times inside a circle in the figure represents the amount of methanol, calculated from the pressure increase, after removing the dry ice; the value agreed with that before the trapping. The

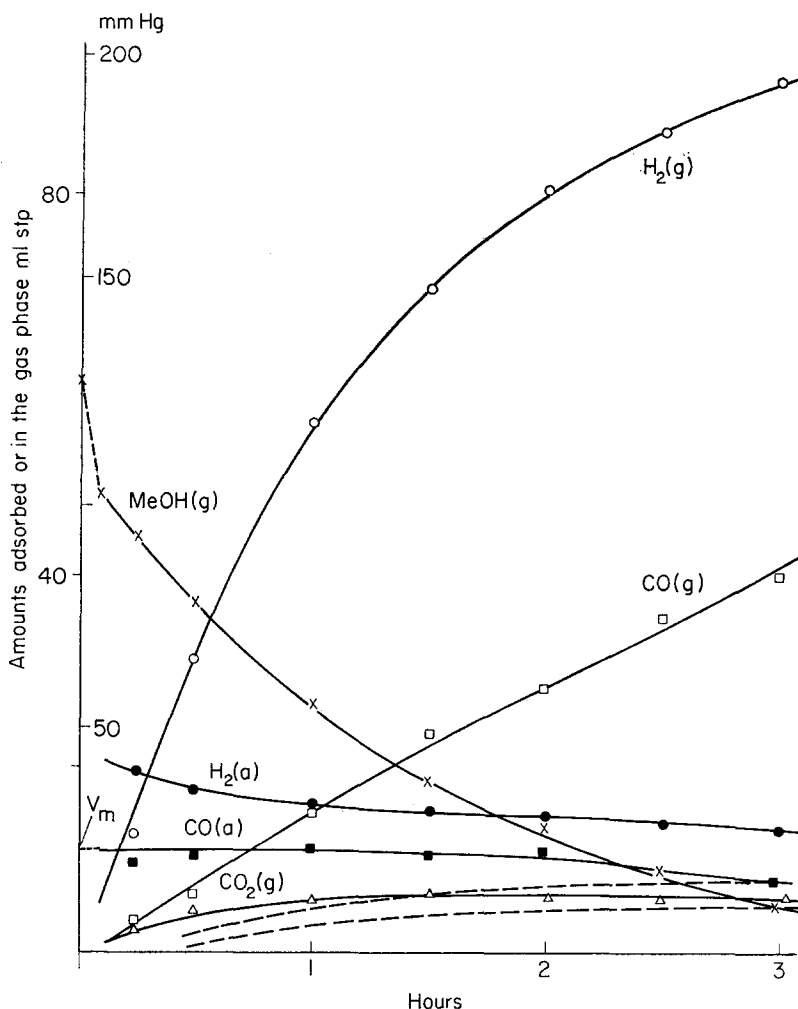


Fig. 2. Adsorption measurements during the methanol decomposition reaction at 250°C when 1.46 g of catalyst was used. Dotted lines represent the amounts of the adsorption of hydrogen (upper line) and carbon monoxide (lower line) in the mixed adsorption of 2H₂:1CO gas.

amount of methanol in the trap was therefore considered to be constant during the trapping with dry ice after instantaneous collection of methanol in the gas phase. In Fig. 4 the results obtained by using liquid nitrogen instead of dry ice are shown.

The results for decomposition of various amounts of methanol are shown in Fig. 5, where the pressure of methanol is plotted against reaction time. The pressures at time zero were, however, estimated from the amounts of methanol introduced and the volume of the reaction system. The initial

decreases in the methanol pressure represented by the upper dotted lines were followed by the linear part of the decreases in the pressure, represented by solid lines. The initial rate of the pressure decrease in the solid line range was almost independent of the methanol pressure; deviation from linearity, however, occurred at a later time.

The surface area of the catalyst was estimated to be 3.5×10^5 cm²/g using the BET method for nitrogen adsorption at -196°C. The apparent activation energy of the methanol decomposition was esti-

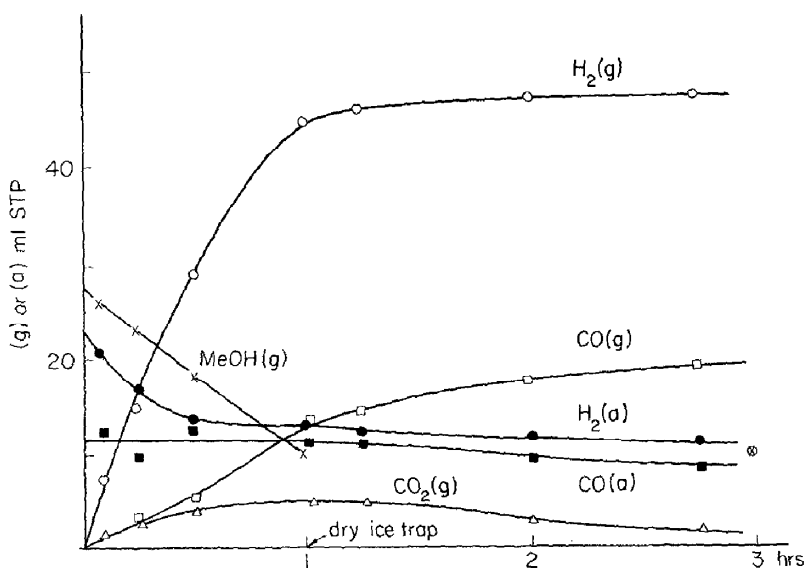


FIG. 3. Effect of elimination of methanol with a Dry Ice trap during the methanol decomposition at 250°C.

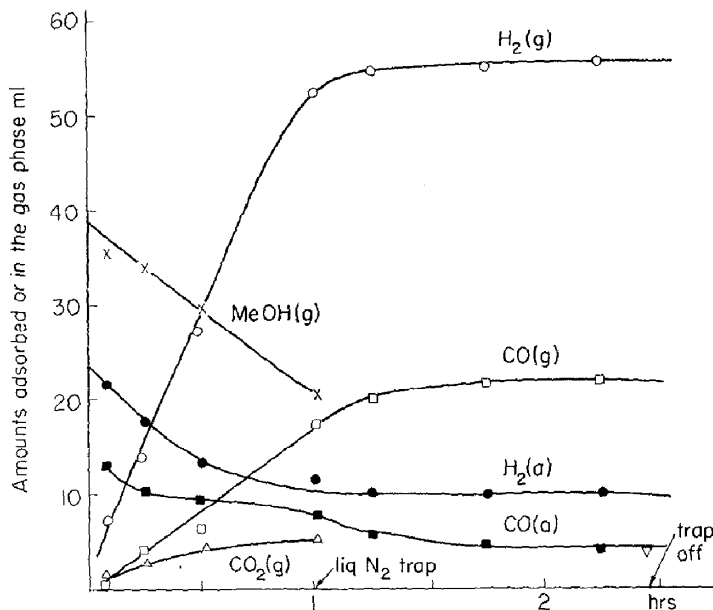


FIG. 4. Elimination effect of methanol and carbon dioxide with a liquid nitrogen trap during the methanol decomposition reaction: ∇ , amount of carbon dioxide when the trap was removed.

mated to be 31.0 kcal/mole from the Arrhenius plots of the zero order reaction constants in the range of 230° to ~280°C.

DISCUSSION

As shown in Figs. 1 and 2, the amounts of adsorption during the decomposition of

methanol were always greater than those in the adsorption from the mixture 2H₂: 1CO, and the former approached the latter as the partial pressures of hydrogen and carbon monoxide increased. The fact suggests that not all the species adsorbed on the catalyst—hydrogen, carbon monoxide,

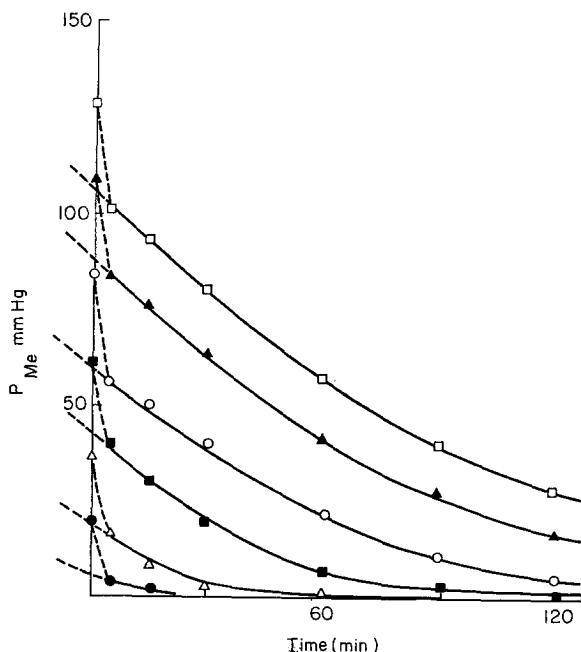


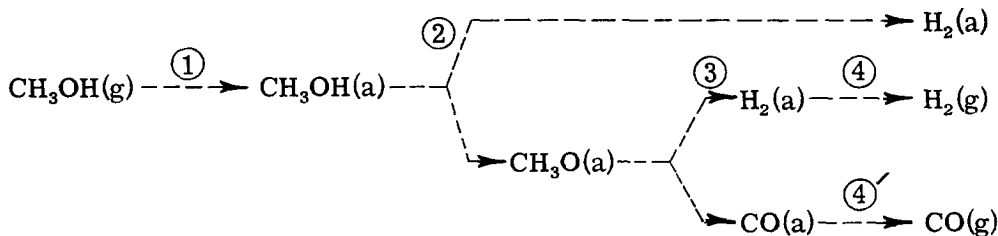
FIG. 5. The methanol decomposition reaction at various initial pressures at 250°C.

and any intermediate complex formed from hydrogen and carbon monoxide—were in equilibrium with hydrogen and carbon monoxide in the gas phase, and that the process of the adsorption of methanol could not be the rate-determining step of the reaction, if we postulate that only one elementary process controls the rate of the overall reaction.

As shown in Fig. 3, the ambient pressure of hydrogen did not decrease when the methanol was abruptly removed from the system during the reaction, and the amount of methanol in the trap stayed constant during the trapping. The facts suggest that the major part of the adsorbed species, hydrogen, carbon monoxide, and the complex formed from them, on the catalyst is not in equilibrium with the methanol in

the gas phase; otherwise, the major part of them would rapidly desorb to be caught by the trap. The processes of the adsorption and desorption of hydrogen and carbon monoxide are accordingly suggested not to be the rate-determining steps of the overall reaction. The suggestion conforms to the previous (7) result that these processes had been shown to be rapid in the case of the synthesis reaction.

Consequently, the rate-determining step is suggested to be the process of the dissociation of adsorbed complex formed from hydrogen and carbon monoxide adsorbed, such as CH_4O and CH_3O . If the decomposition of methanol proceeds as the reverse process of the synthesis reaction previously proposed by the present authors (7), the mechanism would be as follows:



Since the partial pressure of hydrogen did not decrease by trapping, the process (3) in the scheme could not be the rate-determining step, and the process (2) is thus suggested to be the rate-determining step of the reaction.

As shown in Fig. 5, the initial rapid decrease in the methanol pressure represented with the upper dotted lines can be considered to be due to the adsorption of methanol. Hence the order of the methanol decomposition reaction is approximately zero and the rate of the reaction would be roughly expressed by Eq. (1), since the solid lines would show the methanol decomposition reaction

$$r \doteq k \quad (1)$$

The results agree with those observed previously (2, 5); a deviation from linearity, however, was observed at the lower methanol pressure.

As shown in Fig. 2, during the methanol decomposition the ratio of the sum of the amounts of hydrogen adsorbed to that of carbon monoxide adsorbed, which include those in the surface complex formed from them, was nearly 2 at the initial stage, while the sum of the amounts of carbon monoxide adsorbed is nearly equal to the v_m in BET equation. The facts show that the overall stoichiometric formula of the adsorbed species at the initial stage of the reaction is CH₄O, and that the major part of the surface is covered with carbon monoxide which combines with hydrogen. It is accordingly concluded that the catalyst surface is almost fully covered with the adsorbed methanol at the initial stage of the reaction.

A curve considered to be an adsorption isotherm of methanol was obtained as shown with a solid line for 250°C in Fig. 6. The ambient pressure of methanol was obtained by extrapolating the pressure-time curve in Fig. 5 to time zero (lower dotted lines), and the adsorbed amount was estimated from the mass balance between the amount of the methanol introduced and that in the gas phase at that time, because the methanol only adsorbed on the surface. It is thus shown in Figs. 5 and 6 that the

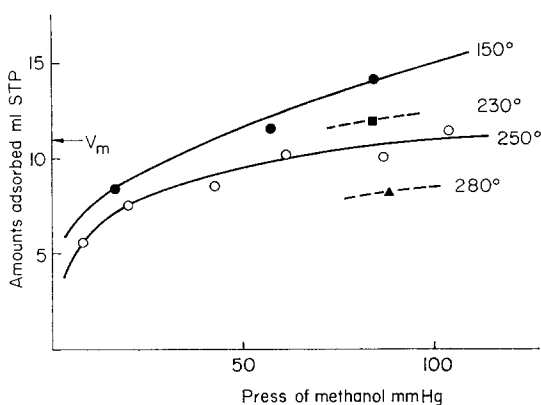


Fig. 6. Relation between adsorbed and gaseous methanol.

nearer the amounts of methanol initially adsorbed approach v_m in the BET equation (see Fig. 6), the nearer the reaction order comes to zero (see Fig. 5). At 150°C the decomposition of methanol was not observed, so the curve was obtained by means of the usual manner for the adsorption measurement.

It is of interest to examine the dependence of the rate of the reaction on the concentration of the adsorbed species. The adsorption during the reaction has generally been estimated from the rate of the overall reaction postulating that an adsorption isotherm, e.g., the Langmuir isotherm, is applicable and that the rate of the reaction is proportional to the surface concentration of the reactants. Such a procedure, however, has no sound basis as long as the postulation has not been verified. The adsorption directly estimated during the reaction should be correlated with the rate of the reaction. It might hardly be possible to distinguish and determine the amounts of a certain species adsorbed on the catalyst from the other when more than two kinds of species are adsorbed, when the amounts of gas adsorbed during the reaction were estimated from the mass balance. In the present case, the amounts of each species adsorbed can be evaluated from those of hydrogen and carbon monoxide adsorbed, supposing that the other species than methanol or an intermediate complex is hardly adsorbed on the surface during

the reaction, taking the empirical formula of the intermediate to be CH_3O as previously (7a) suggested; the supposition would be reasonable at early stage of the reaction. Figure 7 shows the relation between adsorbed and gaseous methanol at an early stage of the reaction at 250°C ; the dotted line gives the curve shown in

methanol as concluded above, Eq. (2) would show the rate of the reaction.

$$r = kA_{\text{Me}} \quad (2)$$

where A_{Me} is the amount of methanol adsorbed and k is the rate constant. The results shown in Fig. 8 support the above conclusion, the solid lines shown in Fig. 7

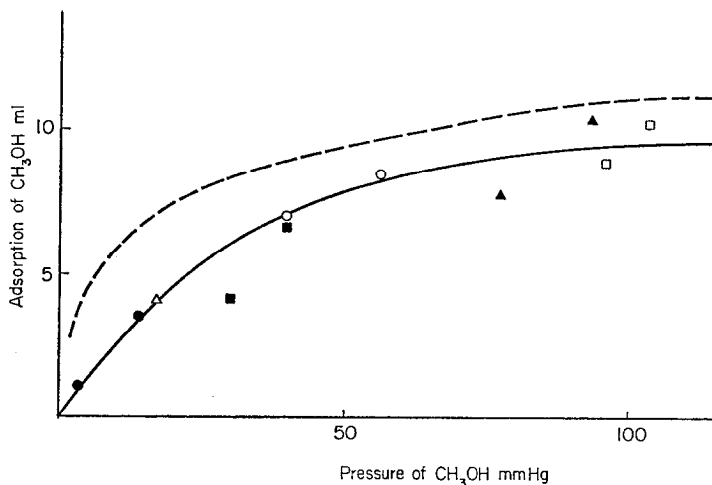


Fig. 7. Relation curve between adsorbed and gaseous methanol during the reaction at an early stage.

Fig. 6, where methanol only was adsorbed on the surface.

Since the reactant of the rate-determining step of the reaction is the adsorbed

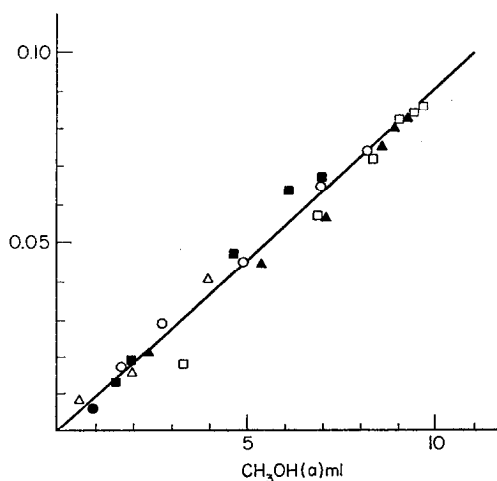


Fig. 8. Relation between CH_3OH (a) and the rate of methanol decomposition reaction at an early stage.

being applied for estimating A_{Me} from P_{Me} .

As for the mechanism and kinetics of the methanol decomposition reaction, it is consequently concluded that the process of the dissociation of the adsorbed methanol into the adsorbed intermediate complex and hydrogen is the rate-determining step of the overall reaction which is the reverse process of the rate-determining step in the synthesis reaction, and that the initial rate of the reaction becomes zero order when the coverage of the adsorbed methanol is almost unity.

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