

Kinetics of Acetaldehyde Hydrogenation Over Silver*

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(Received April 30, 1984)

Abstract

The kinetics of acetaldehyde hydrogenation over silver has been studied by using the steady state and transient response method, at temperatures ranging from 130 to 180°C under atmospheric pressure. The rate expression is

$$r_{\text{EtOH}} = kP_{\text{H}_2}P_{\text{CH}_3\text{CHO}}^{0.44}$$

The analysis of the transient and steady state behavior of the reaction proposes a suitable Eley-Rideal mechanism. The diffuse reflectance infrared fourier transform spectroscopic analysis of the adsorbed species clearly shows acetaldehyde to be weakly adsorbed on the surface during the reaction, and its surface coverage is 0.4–0.7 depending on the concentration of acetaldehyde. The transient response method elucidates the formation of acetic acid and ethyl acetate when the surface oxygen originated from gas flow as an impurity is formed or resides.

1. Introduction

Our previous works^{1–10} have reported on the reactivity and nature of silver: the reaction intermediates formed in the oxidation of ethylene are basically the same as those in the oxidation of acetaldehyde at lower temperatures, 80–180°C. The intermediates consist of three different species, weakly and strongly adsorbed acetaldehyde and the species to form silver acetate. When they are exposed to hydrogen, they can desorb to form alcohol and/or acetic acid. Our interest is next focused on what active sites are available for the two products. The previous papers^{7–10} speculate that surface silver oxide was an active site for the formation of acetic acid and bare silver for the formation of alcohol. In this paper, to confirm the validity of our presumption and to clarify the kinetic structure of the hydrogenation of acetaldehyde, the transient response method and steady state kinetic analysis have been applied. In addition, the adsorbed acetaldehyde is also characterized by the diffuse reflectance infrared fourier transform spectroscopic technique (DRIFTS).

2. Experimental Method

The details of the catalyst preparation and the stabilization of the catalyst can be found elsewhere.^{5,6} The catalyst used for the hydrogenation is the same one as for the oxidation of ethylene, and it is confirmed prior to use that the

* Presented at Chemical Society of Japan Hokkaido regional meeting (1984).

catalyst has sufficient activity and selectivity to ethylene oxide greater than 50%. The composition of the catalyst was 67.6 g-Ag, 0.367 g-K₂SO₄/194.6 g- α -Al₂O₃ and the BET surface area was 0.3 m²/g-Ag. The analysis of gases was conducted by using two gas chromatographs to follow the transient behavior as continuously as possible. Porapack Q column was used for the analysis of acetaldehyde, alcohol, acetic acid and ethyl acetate, and Molecular sieves 5 A column for the analysis of H₂ and O₂.

Acetaldehyde was fed by bubbling He through liquid aldehyde the temperature of which was kept at 0°C. The reactor which was made of Pyrex glass tube was immersed in an oil bath and the bath temperature was excellently controlled within $\pm 0.5^\circ\text{C}$. The total gas flow rate was 160 (± 2) NTP ml/min. The gas composition was changed by using He as a diluent without changing the total flow rate. The residence time in the reactor was less than 17 sec, whereas the transient state of the actual reaction was more than ten minutes. The shift of the experimental response between two inert gas streams He and N₂ from the ideal step function was found within seven seconds, and its response completed 80% of the final level within one second, therefore the mixing effect of gas should be negligible. The schematic diagram of the experimental equipment used is presented in Fig. 1. The transient response method in flow systems has been reviewed in several publications so far, from which one may see its detailed procedure.¹¹⁻¹³⁾

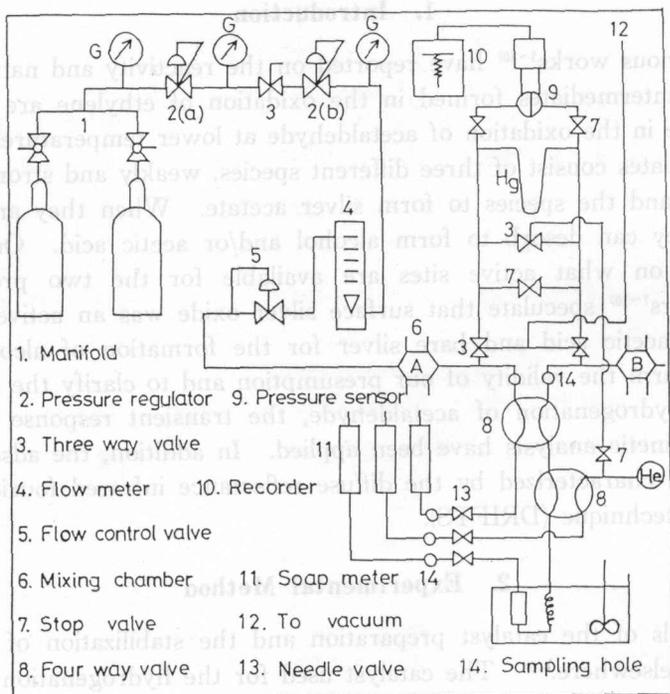


Fig. 1. Schematic diagram of the transient response equipment.

JIR-40X and DRA 11 (JEOL) are used for the diffuse reflectance infrared fourier transform spectroscopy, and details of the flow IR cell in which adsorbed species can be directly detected during the reaction will be found in ref. 14. The flow cell is carefully constructed so as to eliminate the absorption of IR in gas phase, as the space of the gas phase in the cell is so little as to be less than 0.2 cc (see ref. 14). About 20 mg of KBr powder containing 2 wt.% silver catalyst is put on the sample holder.

3. Experimental results and Discussion

3-1. Transient Behavior of Acetaldehyde Hydrogenation

Fig. 2 shows the $\text{CH}_3\text{CHO}(\text{dec., } 0)\text{-CH}_3\text{CHO}$ response during the hydrogenation of aldehyde. The response clearly demonstrates a delay indicating the desorption of adsorbed aldehyde, and the steep decay of the curve shows its weak adsorption on the surface. The graphical integration of the curve evaluates its adsorbed amount to be 6.0×10^{-7} mol/g-Ag (1.2×10^{14} molecules/cm²), which corresponds to 0.09 of the surface coverage, based on the total surface silver atoms, 1.3×10^{15} /cm².¹⁵⁾ From this calculation, it may be recognized that part of the surface during the reaction should be covered with the weakly adsorbed aldehyde. On the other hand, the $\text{H}_2(\text{dec., } 0)\text{-H}_2$ response instantaneously responds to nil, indicating no adsorption of H_2 .

After the surface had been oxidized in the $\text{O}_2\text{-He}$ stream for 12 hours (Run 1), the surface was reduced by H_2 for one hour (Run 2), then a $\text{CH}_3\text{CHO-}$

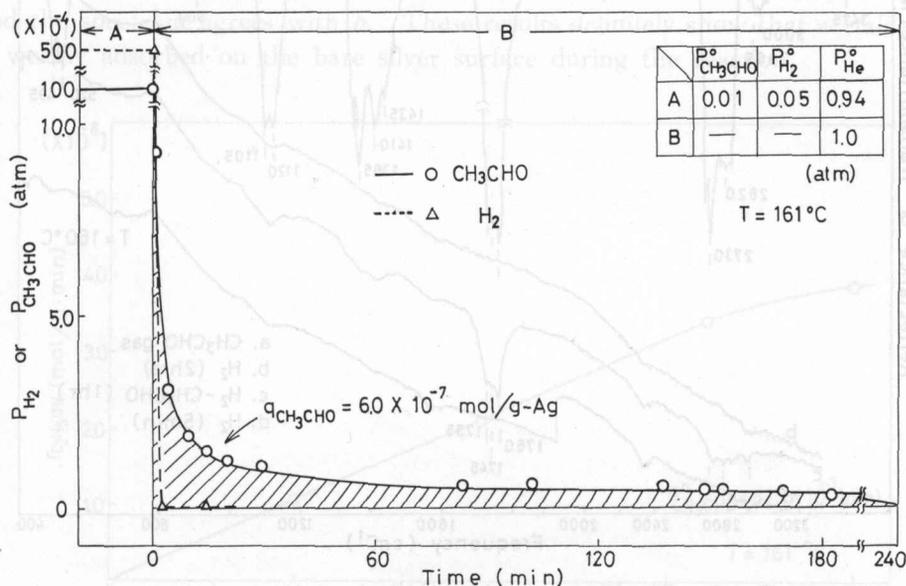


Fig. 2. The responses of acetaldehyde and hydrogen in the outlet stream caused by the step decrease of the concentration of acetaldehyde and hydrogen in the inlet stream.

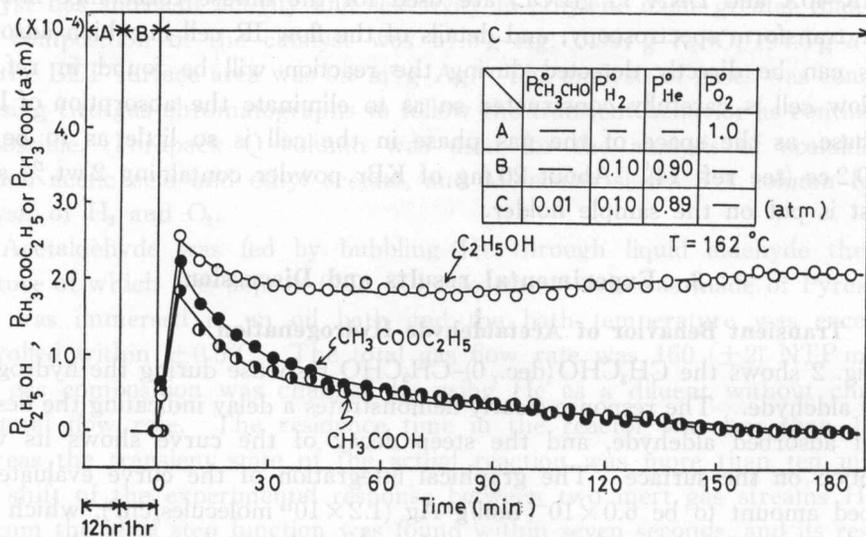


Fig. 3. The responses of alcohol, acetic acid and ethyl acetate in the outlet stream caused by the step increase of the concentration of acetaldehyde and hydrogen in the inlet stream.

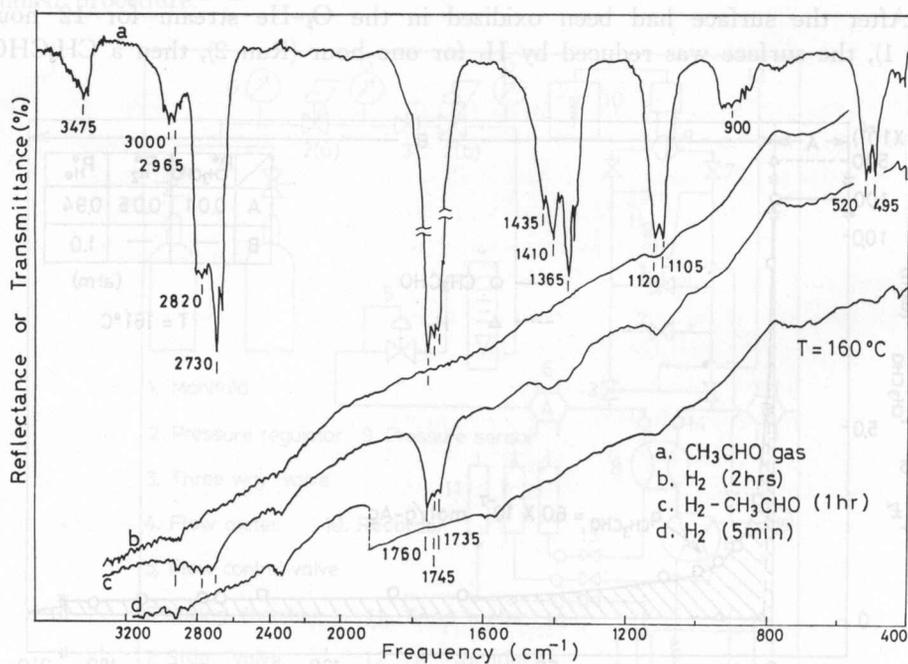


Fig. 4. The IR spectra of acetaldehyde adsorbed on a bare silver surface by the diffuse reflectance infrared fourier transform spectroscopic technique.

H_2 -He mixture was fed with stepwise fashion without changing the total gas flow rate (Run 3). Thus, Fig. 3 clearly exhibits the formation of ethyl alcohol, acetic acid and ethyl acetate in which the latter two disappeared within three hours. It can reasonably be presumed that the acetic acid is formed by the reaction of acetaldehyde with surface oxygen which resides due to the brief reduction of the surface with H_2 (Run 2). On the other hand, ethyl acetate is formed by the reaction between the acetic acid and the ethanol produced. These presumptions can be supported by the successive experimental findings: after Run 3 in Fig. 3, the repetition between Runs 2 and 3 clearly exhibits only the formation of ethanol with no production of acetic acid or ethyl acetate. From these results, one may recognize that alcohol should be formed on a bare silver surface and acetic acid on an oxidized surface.

3-2. DRIFTS in Acetaldehyde Hydrogenation

Fig. 4 illustrates the diffuse reflectance infrared fourier transform spectra of the adsorbed species during the hydrogenation. *a* is an IR spectrum of gaseous acetaldehyde in a gas cell, which is expressed in transmittance, *b* is an IR spectrum of the sample reduced with a H_2 stream at 161 C. After *b*, the CH_3CHO-H_2 mixture is introduced into the IR cell for 1 hr and the spectrum *c* is followed. In the spectrum *c*, the absorption bands in the regions 1735-1760, 2730-2820 and 2965-3000 cm^{-1} may easily be assigned as C=O, CH of CHO and CH_3 , respectively, by comparing with gaseous acetaldehyde spectrum *a*. The CH_3CHO-H_2 mixture is changed into a pure He stream with a stepwise fashion and spectrum *d* is followed. In *d*, the characteristic absorption bands quickly disappear and the spectrum agrees with *b*. These results definitely show that acetaldehyde is weakly adsorbed on the bare silver surface during the reaction.

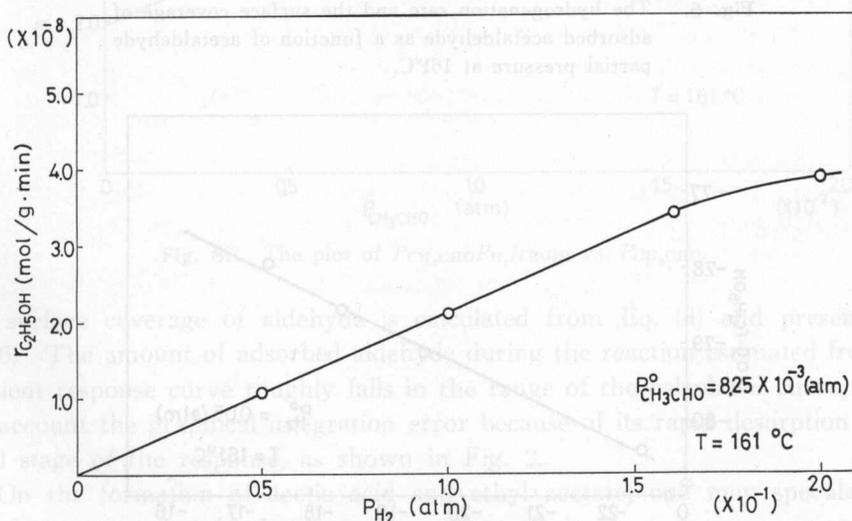


Fig. 5. The hydrogenation rate as a function of hydrogen partial pressure at 161°C.

3-3. Steady State Kinetics

The hydrogenation rate obeys the first order kinetics with respect to the partial pressure of H_2 and the Langmuir type kinetics with respect to CH_3CHO as shown in Figs. 5 and 6, respectively. As is shown in Fig. 7, the overall reaction rate is expressed as

$$r_{EtOH} = kP_{H_2}P_{CH_3CHO}^{0.44} \quad (1)$$

On the basis of the experimental data presented above and Boreskov et al's reports,^{16,17)} one could propose the following reaction model;

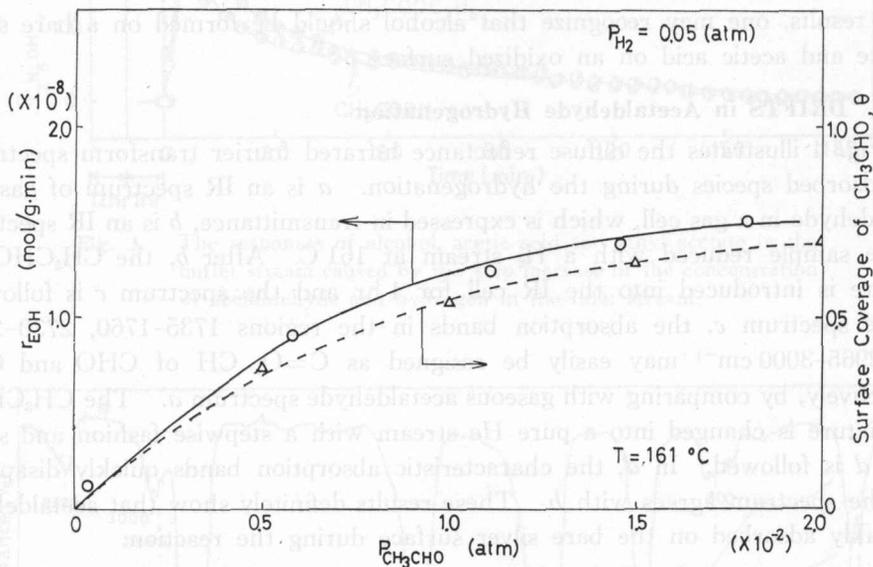


Fig. 6. The hydrogenation rate and the surface coverage of adsorbed acetaldehyde as a function of acetaldehyde partial pressure at 161°C.

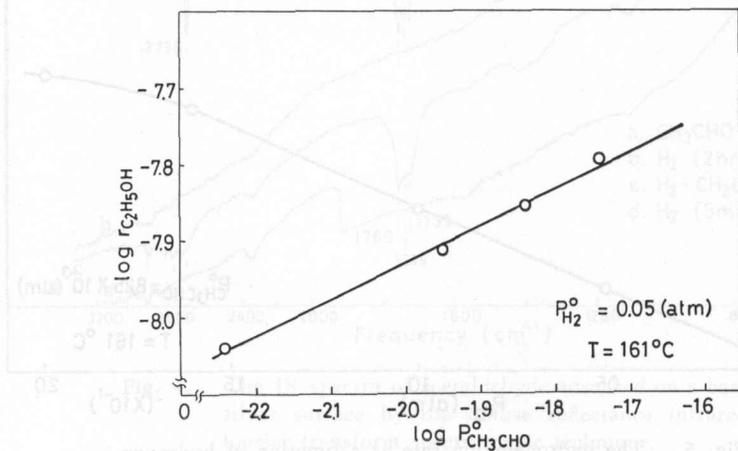
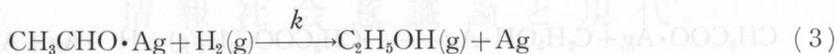


Fig. 7. The plot of $\log r_{EtOH}$ vs. $\log P_{CH_3CHO}$.



The steady state rate expression thus can be proposed as follows,

$$r_{\text{EtH}} = \frac{kK P_{\text{CH}_3\text{CHO}} P_{\text{H}_2}}{1 + K P_{\text{CH}_3\text{CHO}}} \quad (4)$$

Equation (4) may be rewritten

$$\frac{P_{\text{CH}_3\text{CHO}} P_{\text{H}_2}}{r_{\text{EtOH}}} = \frac{1}{kK} + \frac{P_{\text{CH}_3\text{CHO}}}{k} \quad (5)$$

$P_{\text{CH}_3\text{CHO}} P_{\text{H}_2} / r_{\text{EtOH}}$ is plotted as a function of $P_{\text{CH}_3\text{CHO}}$ and a good straight line is obtained as shown in Fig. 8. The intercept and the slope of the straight line give

$$k = 4.4(\pm 0.1) \times 10^{-7} \text{ mol. g-Ag.}^{-1} \text{ min.}^{-1} \text{ atm.}^{-1} \quad \text{and} \quad K = 116(\pm 10) \text{ atm}^{-1}$$

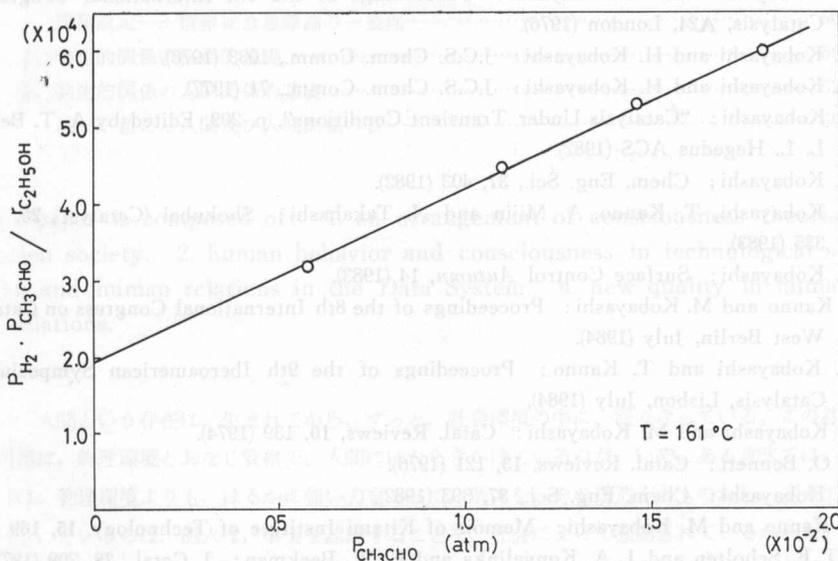
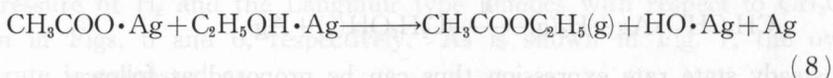
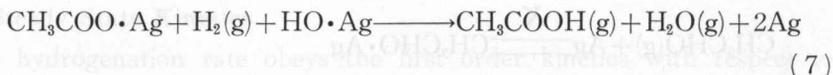


Fig. 8. The plot of $P_{\text{CH}_3\text{CHO}} P_{\text{H}_2} / r_{\text{EtOH}}$ vs. $P_{\text{CH}_3\text{CHO}}$.

The surface coverage of aldehyde is calculated from Eq. (4) and presented in Fig. 6. The amount of adsorbed aldehyde during the reaction estimated from the transient response curve roughly falls in the range of the calculated curve, taking into account the graphical integration error because of its rapid desorption at the initial stage of the response, as shown in Fig. 2.

On the formation of acetic acid and ethyl acetate, one may speculate the following reaction mechanism.





4. Conclusions

Acetaldehyde is steadily hydrogenated on bare silver surface. When surface oxygen species exists, even in a small amount, acetic acid and ethyl acetate are formed with ethyl alcohol. The hydrogenation is progressed by the reaction between weakly adsorbed aldehyde and gaseous hydrogen. The weakly adsorbed acetaldehyde is clearly recognized by DRIFTS comparing the absorption bands in gaseous one.

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