JOURNAL OF CATALYSIS **94**, 353–359 (1985)

The Behavior of Surface Formate Ions as Reaction Intermediates in the Decomposition of Methanol over Cr_2O_3

KOU YAMASHITA, SHUICHI NAITO, AND KENZI TAMARU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan

Received July 18, 1984; revised January 5, 1985

The mechanism of the decomposition of methanol over Cr_2O_3 was studied by *in situ* infrared spectroscopy and by a tracer jump method. The stability of surface formate ions formed by the decomposition of methanol over Cr_2O_3 greatly depended on the reaction conditions. In the presence of methanol vapor, surface formate decomposes easily to H_2, CO, and CO_2, with an activation energy of 29 kcal mol^{-1}, although it is quite stable under vacuum ($E_a = 46$ kcal mol^{-1}). The infrared absorption bands of the formate ions are shifted in the presence of methanol vapor, suggesting some chemical interaction between formate ions and adsorbed methanol. By isotope-labeling experiments it was confirmed that the formate ion, observed by infrared spectroscopy, is the reaction intermediate of methanol decomposition in spite of its marked stability in the absence of methanol.

INTRODUCTION

It is well known that the surface formate ion is formed when methanol is adsorbed on various metal oxides such as alumina (*1–4*), magnesia (*5–7*), and zinc oxide (*8*) at elevated temperatures, although its stability largely depends on the oxide employed. On alumina (*9*) it has been revealed that formate ion is not a reaction intermediate for alcohol or formic acid decomposition reaction, but on magnesia or zinc oxide (*10*) it could be incorporated into the decomposition reaction to form H_2, CO, and CO_2. Accordingly, it is interesting to investigate the nature of the formate ions on various oxides and their dynamic behavior during the decomposition of alcohol or formic acid.

In this study, infrared spectroscopic analysis and an isotope jump method were employed to investigate the behavior of surface formate ions formed during the decomposition of methanol over Cr_2O_3, which is one of the components of the practical methanol synthesis catalysts. Surface formate ions on Cr_2O_3 could be easily formed by the interaction of formic acid or methanol, or by the CO–H_2 reaction at elevated temperatures. However, their stability is quite sensitive to the ambient gases and, in the presence of gaseous methanol, the decomposition of formate ions was accelerated remarkably compared to that under vacuum. This phenomenon was investigated in more detail in connection with the mechanism of the methanol decomposition reaction over Cr_2O_3.

EXPERIMENTAL

Cr_2O_3 was prepared by thermal decomposition of $(NH_4)_2Cr_2O_7$ (Wako Chemicals) to a similar method used by Zecchina *et al.* (*11*). The decomposition product was treated with oxygen at 400°C for several hours to obtain green crystallized α-Cr_2O_3. After washing with water and drying, 40 mg of the catalyst was pressed into a disk of 2 cm in diameter, and placed in an infrared cell which was connected to a closed gas-circulation system. Another 1.0 g of the catalyst was placed in a reactor connected to the same system, for the purpose of simultaneous measurements of the reaction rate and the infrared spectrum.

Before each run the catalyst was treated

0021-9517/85 $3.00

with oxygen at 450°C for 1 h, then reduced with hydrogen for 1 h at 450°C and evacuated for 1 h also at 450°C. CD_3OD (99% purity of deuterium) was mainly employed as a reactant because of the poor transmittance of Cr_2O_3 in the region above 2500 cm^{-1}. ^{13}CO, which contains 90% carbon 13, was used for labeled experiments. Surface species adsorbed on catalysts during the reaction were observed by infrared spectroscopy, using a Jasco IRA-1B grating spectrophotometer and a JEOL JIR-10 Fourier-transform infrared spectrometer. The reaction products were separated into three parts by using liquid-nitrogen and dry ice–methanol cold traps, and analyzed by gas chromatography using molecular sieve 5A and Porapack Q. In the experiment using isotopes, a mass spectrometer was used to determine the isotope distribution in the reaction products. The amounts of adsorbed species were estimated by infrared spectroscopy using the following extinction coefficients; for methoxy group, $\nu_s(C-H) =$ 1.2 cm^3/absorbance, and for $\nu_{as}(O-C-O) =$ 0.18 cm^3/absorbance. These absorption coefficients were obtained from the separate adsorption measurements using a larger amount of catalysts.

RESULTS

1. Reaction Products of the Decomposition of Methanol on Cr_2O_3

When methanol vapor was introduced on Cr_2O_3 in the temperature range 200 to 400°C, the main decomposition products were H_2, CO, CO_2, and CH_4, together with CH_3OCH_3. At temperatures higher than 350°C, small amounts of C_2H_4 and C_2H_6 were detected in the products. The ratio of CO/CO + CO_2 in the products varied from 30 to 70%, depending on the oxidation state of the catalyst surface. CO selectivity was increased to some extent when the reaction was continued for a longer period but it did not exceed 80%. The amount of CH_4 was about one order of magnitude less than that of CO_2 at lower temperatures, but became comparable at high temperatures.

2. Surface Species during the Reaction

The infrared spectra of adsorbed species on Cr_2O_3 during the course of the CD_3OD decomposition reaction at 300°C are shown in Fig. 1. Before spectra were taken, the infrared cell was cooled from reaction temperature to room temperature in the presence of methanol vapor, and then methanol was removed with a liquid-nitrogen cold trap. In addition to the C–D stretching bands of the surface methoxy group at 2064 and 2214 cm^{-1}, three bands were observed at 2160, 1573, and 1337 cm^{-1}. When methanol vapor was trapped and decomposition was continued for a longer period, these three bands were shifted to 2184, 1548, and 1329 cm^{-1}, respectively. From the position and the shape of these three bands, they may be assigned to the surface formate species on Cr_2O_3, which was confirmed by the introduction of DCOOD onto the clean Cr_2O_3 catalyst. Formic acid is well known to dissociate on Cr_2O_3 at room temperature, forming formate species as shown in Fig. 2, whose bands were also shifted by the introduction of gaseous methanol. From the comparison of bands of surface species formed by CD_3OD decomposition with those formed by DCOOD adsorption, it

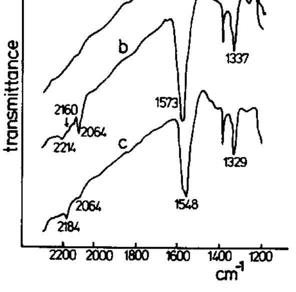

FIG. 1. Infrared spectra of the adsorbed species during CD_3OD decomposition over Cr_2O_3. (a) Background; (b) CD_3OD decomposition at 300°C for 2 h; and (c) after (b), CD_3O (a) decomposition was continued for 15 h, with liquid N_2 cold trap.

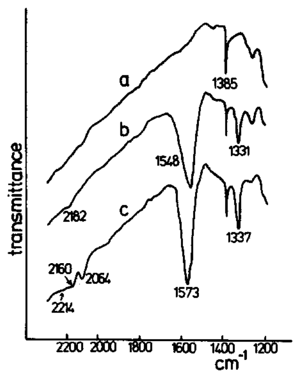

FIG. 2. Infrared spectra of the adsorbed species after the introduction of DCOOD over Cr_2O_3. (a) Background; (b) DCOOD adsorption at 200°C; and (c) after (b), CD_3OD vapor was introduced in the gas phase.

was confirmed that formate species was formed on Cr_2O_3 surface during methanol decomposition reaction. The IR bands of formate ion on Cr_2O_3 shifted by the presence of methanol and restored to their original wavenumbers in its absence.

Formate species was similarly formed by $CO-H_2$ reaction over Cr_2O_3 which is known as a component of practical methanol synthesis catalyst. But in this experiment, it revealed very low activity for methanol formation although main surface species was formate ion with a small amount of methoxy species during the $CO-H_2$ reaction. This result suggests that the formation of formate ion in the $CO-H_2$ reaction is easy.

3. *Dynamic Behavior of Formate Ions*

To investigate the role of the formate ion on Cr_2O_3 in the steady-state methanol decomposition reaction, isotope-labeling experiments were carried out by the use of ^{13}C. The procedure was as follows.

(i) $D^{13}COO(a)$ was prepared by the $^{13}CO-D_2$ reaction at 300°C for 2 h, the amount obtained was as that formed by methanol decomposition reaction, but the amount of methoxy species was much less.

(ii) After the removal of ^{13}CO by evacuation, $^{12}CD_3OD$ was introduced and the reaction was started.

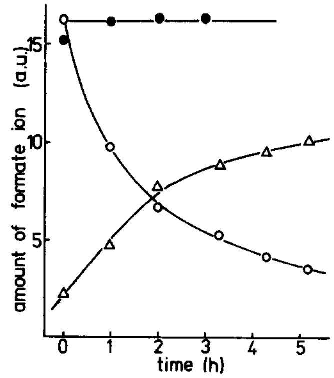

FIG. 3. Time courses of the decomposition of the surface formate, prepared by $^{13}CO-D_2$ reaction over Cr_2O_3 at 573 K for 1 h. (●) Amount of $D^{13}COO(a)$ under evacuation at 533 K. (○) Amount of $D^{13}COO(a)$ during the circulation of $^{12}CD_3OD$ at 533 K. (△) Amount of $D^{12}COO(a)$ during the circulation of $^{12}CD_3OD$ at 533 K.

The results are shown in Fig. 3. It is very interesting to note that [^{13}C]formate prepared by procedure (i) was stable and hardly decomposed in the absence of methanol vapor (closed circle). However, in the presence of methanol it reacted readily and was washed away by ^{12}C species (open circle) and [^{12}C]formate appeared instead of [^{13}C]formate. Accordingly, the presence of methanol vapor not only shifted the infrared band of formate ion, but also made it more reactive and changed its kinetic behavior.

During the substitution of [^{13}C]formate by [^{12}C]formate, ^{13}CO, and $^{13}CO_2$ were observed in the decomposition products, although $^{13}CH_4$, $^{13}CD_3O^{13}CD_3$, $^{13}CD_3OD$, and $^{13}CD_3O(a)$ were not appreciable. Total amount of ^{13}C in the products was almost as much as that of ^{13}C which disappeared from the catalyst surface, as shown in Table 1. From these observations, it is concluded that the decomposition of methanol proceeds through formate ions which decompose to reaction products over Cr_2O_3.

4. *Kinetics of Formate Ion Decomposition*

As has been demonstrated in the previous section, the formate ion decomposition step seems to be one of the elementary

TABLE 1

$D^{12}COOD$ Decomposition Reaction over $D^{13}COO(a)$ Preadsorbed Cr_2O_3 Surface

Reaction temp. (°C)	Reaction time (h)	[^{13}C]Formate (%) on the surface		Total ^{13}C in the products (cm^3 × 10^3)	Decomposed [^{13}C]formate (cm^3 × 10^3)
		Before	After		
276	1.0	90	40	14.6 ± 2.2	16.2 ± 1.8
276	1.1	40	30	4.7 ± 1.1	5.0 ± 1.8
250	4.0	78	50	13.2 ± 1.6	11.0 ± 1.8

steps in methanol decomposition reaction on Cr_2O_3. Accordingly, the kinetics of this step was studied in more detail. To investigate the dependence of the decomposition rate of formate ion upon the concentration of formate ion itself, methanol decomposition was carried out and the rate of CO + CO_2 formation was determined at various amounts of surface formate. As shown in Fig. 4, the rate of CO + CO_2 formation exhibited a good correlation with the amount of formate, and the first-order decomposition of formate was observed.

The first-order rate constants of formate ion decomposition can be determined from the plots of logarithm of the amount of formate ion versus reaction time at various temperatures, whose Arrhenius plots give activation energy (E_a) and frequency factors of formate ion decomposition. The results are shown in Fig. 5 for the decomposition reactions of formate ion in the presence of methanol and under vacuum. In the absence of methanol the decomposition of formate ion required high E_a of 46 kcal mol^{-1}, but in the presence of methanol or during methanol decomposition, E_a was decreased to 29 kcal mol^{-1}. The frequency factor was also different between these two cases, and was larger under vacuum (log A = 16.0 h^{-1}) than in the presence of methanol vapor (log A = 11.3 h^{-1}). Such difference is interpreted to be due to the different mechanisms of formate ion decomposition in the cases with and without methanol, suggesting the participation of methanol in the decomposition of formate ion.

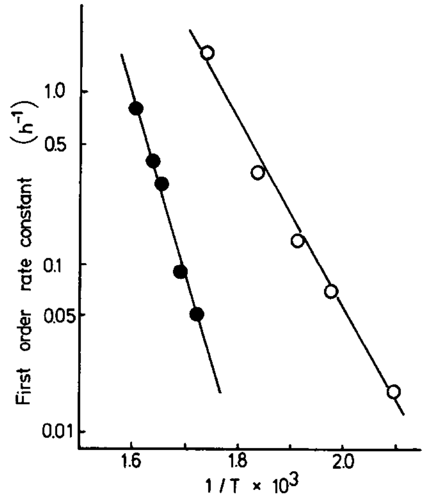

FIG. 5. Arrhenius plots of the first-order rate constants of the decomposition of surface formate: (○) in the presence of gaseous CD_3OD and (●) thermal decomposition under vacuum.

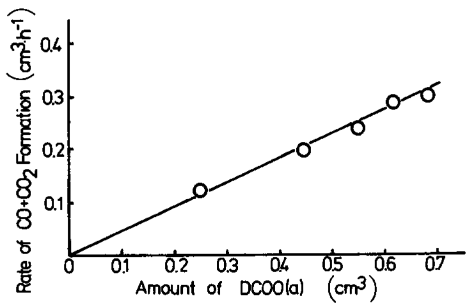

FIG. 4. Dependence of the rate of CO + CO_2 formation upon the amount of DCOO(a) during CD_3OD decomposition over Cr_2O_3 at 250°C.

5. *The Dependence of the Rate of Methanol Decomposition upon Its Pressure*

On the basis of the results described above, it is strongly suggested that methanol vapor plays an important role in the reaction. The following experiments were carried out to study the effect of methanol pressure on the reaction. Figure 6 shows the methanol pressure dependence of the rate of the reaction and also that of the amount of surface methoxy group and surface formate. The rates of D_2 and CO +

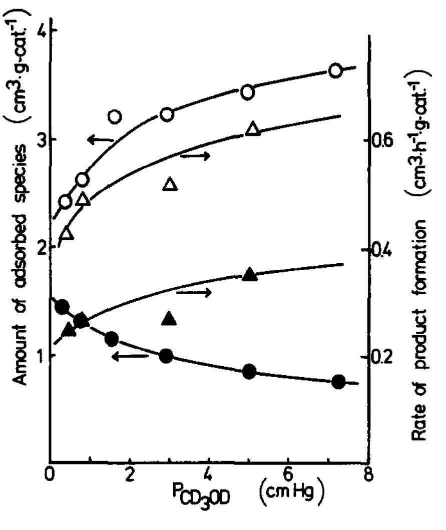

FIG. 6. Methanol pressure dependences of the rate and the amount of the surface species during CD_3OD decomposition over Cr_2O_3 at 260°C. (△) Rate of D_2 formation, (▲) rate of CO + CO_2 formation, (○) amount of $CD_3O(a)$, and (●) amount of DCOO(a).

CO_2 formation increased to some extent by increasing the pressure of methanol, but the amount of formate ion decreased by increasing methanol pressure, although it is an intermediate species of the reaction. On the other hand, the amount of methoxide, to which the rate of the reaction is seemingly proportional, was increased by methanol addition.

The results of methanol pressure-jump experiments from 32 to 0 Torr is shown in Fig. 7. At first, methanol decomposition was allowed to continue in order to reach a steady state at 260°C. Prior to the pressure jump, the reaction system was evacuated at room temperature or at about 80°C for 2 h, so as to remove physically adsorbed methanol on the catalyst and on the glass wall. Then the cold trap was cooled by liquid nitrogen to keep the methanol pressure at zero, and the catalyst temperature was raised to 260°C. The decomposition of surface formate ion to form CO and CO_2 proceeded at about the same rate as that in the steady state for about 15 min, but after that the rate decreased abruptly. During this period, the infrared band of formate ion was shifted to a lower wavenumber, and after that the decomposition of formate ion was stopped.

On the other hand, when methanol vapor was kept at 0 Torr, the amount of surface methoxy group decreased and that of formate ion increased, accompanied by the formation of an excess amount of hydrogen. The excess formation of hydrogen can be explained by the amount of methoxide which converted to formate.

This phenomenon was reversible, that is, when the methanol vapor was introduced again, the amount of formate ion decreased and that of methoxide increased instead to restore the previous steady-state surface composition, accompanying the evolution of H_2, CO, and CO_2. These results are consistent with those of the methanol pressure dependence as shown in Fig. 6 already.

The rate of methane formation was also markedly increased when methanol vapor was removed, suggesting the inhibition of methane formation by methanol vapor.

DISCUSSION

In the case of methanol decomposition

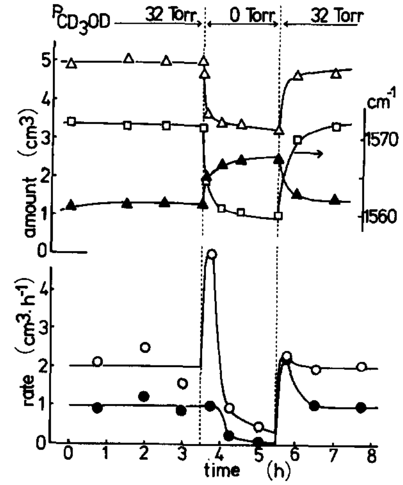

FIG. 7. Effect of methanol pressure on the reaction rates and the amount of the adsorbed species at 260°C. (○) Rate of D_2 formation, (●) rate of CO + CO_2 formation, (△) amount of $CD_3O(a)$, (▲) amount of DCOO(a), and (□) peak position of the asy. (O–C–O) of the adsorbed formate ion.

over Cr_2O_3, the main reaction is a well-known simple dehydrogenation of methanol, $CH_3OH \rightarrow CO + 2H_2$. In addition, a dehydration reaction occurs at the acidic sites on Cr_2O_3, and ether and water are formed

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

In addition, C_2H_4 may be formed at higher temperatures from CH_3OCH_3, and C_2H_6 by its hydrogenation.

It is more difficult to explain the formation of CO_2 and CH_4. Part of CO_2 may be formed by the secondary water-gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2,$$

but another part of CO_2 could be formed directly by the decomposition of formate ion. The dehydrogenation of methanol may proceed as

$$\begin{aligned} CH_3OH &\rightarrow CH_3O(a) + H(a), \\ CH_3O(a) + O(s) &\rightarrow HCOO(a) + H_2, \\ HCOO(a) &\rightarrow CO + \tfrac{1}{2}H_2 + O(s) \\ &\qquad \text{or } CO_2 + \tfrac{1}{2}H_2, \end{aligned}$$

where O(s) represents some surface oxygen on Cr_2O_3. In the case of CO_2 evolution from formate, O(s) is incorporated into CO_2 and the catalyst surface is consequently reduced. On such reduced surfaces, methane may be formed from the methanol leaving one oxygen atom on the surface as

$$CH_3OH \rightarrow CH_4 + O(s)$$

Thus it is proposed that CO_2 and CH_4 are formed as a result of the following two sequential reactions involving O(s),

$$\begin{array}{l} CH_3OH + O(s) \rightarrow CO_2 + 2H_2 \\ \underline{\quad CH_3OH \rightarrow CH_4 + O(s) \quad} \\ 2CH_3OH \rightarrow CH_4 + CO_2 + 2H_2 \end{array}$$

This equation is supported by the fact that at higher temperatures the rate of CH_4/CO_2 approaches unity.

The main reaction, that is the dehydrogenation of methanol, may consist of three major steps as follows,

$$CH_3OH(g) \xrightarrow{\text{step 1}} CH_3O(a) \xrightarrow{\text{step 2}} HCOO(a) \xrightarrow{\text{step 3}} CO, CO_2$$

The first step is the dissociative adsorption of methanol on Cr_2O_3 surface, which is very rapid when such sites are available. The second step is the formation of formate ion from surface methoxide, and the third one is the decomposition of formate into CO or CO_2. From the results in Fig. 6, it is suggested that the rate of the second step does not depend on the methanol pressure, but that the third step has a positive dependence on methanol pressure. Consequently, the steady-state reaction rate can be expressed as

$$V = k_2(\text{methoxide}) = k_3(\text{formate})P^n_{CH_3OH}.$$

At the steady state of the overall reaction, the rate of step 2 is equal to that of step 3, and the relative coverage of methoxide/formate is determined by the equation above. If the methanol pressure is increased, the rate of step 3 will become correspondingly larger than that of step 2, and consequently formate ion will decrease and methoxy group will increase simultaneously, resulting in the new steady-state surface composition. The methanol pressure dependence of the rate of step 3 may be interpreted as due to the direct effect of either methanol vapor or adsorbed methanol which is in equilibrium with gaseous methanol under the reaction condition. From the results of Fig. 7 it is confirmed that the latter is the case. Such adsorbed methanol could not be removed by evacuation at room temperature, which suggests that it is not a weak physical adsorption but more strongly held methanol which takes place. When the evacuation temperature was raised to 150°C, part of the adsorbed methanol which participates in the decomposition of formate ion was removed from the surface, but most of them remained on the surface.

In order to examine the relation between the adsorbed alcohol and the infrared band of formate ion under the reaction condition

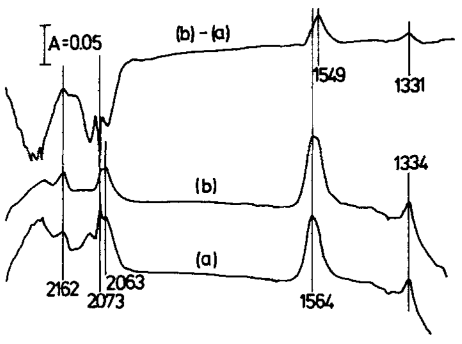

FIG. 8. Fourier-transform infrared spectra of adsorbed formate ion during CD_3OD decomposition at 270°C. (a) P_{CD_3OD} = 7.5 Torr, (b) P_{CD_3OD} = 1.5 Torr.

at 270°C, FT-IR spectra were recorded at methanol pressures of 7.5 and 1.5 Torr, as shown in Fig. 8. When the methanol pressure is decreased to remove part of the adsorbed methanol, some amount of formate ion, which has an adsorption band at 1549 cm^{-1}, appeared. This observation suggests that adsorbed states of formate ions in the presence and absence of adsorbed methanol are different, and the former is easily decomposed to CO and CO_2, whereas the other is quite stable.

The chemical nature of the adsorbed methanol and the interaction between the adsorbed methanol and formate ion may be interpreted as an "associated effect," and the following speculation would be possible. According to the literature, Cr_2O_3 catalyst prepared by the method in this study, is presumed to expose (001) surface. If this is the case, one Cr^{3+} cation center has three coordination sites on the surface. The formate ion needs two of them and one site is available for surface methoxy group. When a methoxy group is coordinated to the same Cr^{3+} with a formate ion, the formate ion may be electronically affected by the methoxy group, which possesses an electron-donating property, and causes a facile decomposition of the formate ion.

REFERENCES

1. Kagel, R. O., *J. Phys. Chem.* **71**, 844 (1967).
2. Deo, A. V., and Dalla Lana, I. G., *J. Phys. Chem.* **73**, 716 (1969).
3. Hertl, W., and Cuenca, A. M., *J. Phys. Chem.* **77**, 1120 (1973).
4. Knözinger, H., and Stubner, B., *J. Phys. Chem.* **82**, 1526 (1978).
5. Kagel, R. O., and Greenler, R. G., *J. Chem. Phys.* **49**, 1638 (1968).
6. Tench, A. J., Giles, D., and Kibblewhite, J. F. J., *Trans. Faraday Soc.* **67**, 854 (1971).
7. Bowker, M., Houghtow, H., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **77**, 3023 (1981).
8. Ueno, A., Onishi, T., and Tamaru, K., *Bull. Chem. Soc. Jpn.* **43**, 2652 (1970).
9. Noto, Y., Fukuda, K., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **63**, 2300 (1967).
10. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **67**, 3585 (1971).
11. Zecchina, A., Coluccia, S., Guglielminotti, E., and Ghiotti, G., *J. Phys. Chem.* **75**, 2774 (1971).