Dynamic Technique to Elucidate the Reaction Intermediate in Surface Catalysis

Water-Gas Shift Reaction

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The mechanism of the water-gas shift reaction on ZnO and MgO was studied by means of infra-red spectroscopy during the course of the reaction. When a mixture of carbon dioxide and hydrogen was introduced over ZnO, formate ion was observed. The rate of decomposition (dehydration) of the surface formate ion was measured at the reaction temperature (230°C) as a function of its concentration, and compared with the rate of the overall reaction on ZnO at the same coverage of the surface formate ion. Both rates were in reasonable agreement showing that the surface formate is the reaction intermediate of the water-gas shift reaction on ZnO and its decomposition is the rate-determining step.

When a mixture of carbon monoxide and water vapour was passed over MgO, the formation of surface formate ion was similarly confirmed. It was, however, different from ZnO, in that it was difficult to detect the surface formate ion from a mixture of carbon dioxide and hydrogen. The comparison of the rate of the dehydrogenation decomposition of the surface formate ion with that of the overall reactions at the same formate coverage leads to conclusion that the surface formate ion is the reaction intermediate of the water-gas shift reaction on MgO and the rate determining step is the dehydrogenation of the formate ion.

The mechanism of the water-gas shift reaction has been studied by many workers on various catalysts and has been discussed on the basis of the reaction kinetics; this resulted in various mechanisms inconsistent with each other.[1-6] Scholten and his coworkers [1] observed the formation of formate ion by infra-red spectroscopy when a mixture of carbon monoxide and water vapour was introduced over magnesium oxide, and they concluded that the formate ion is the reaction intermediate of the water-gas shift reaction on MgO. However, even if the adsorbed species was present on the catalyst during the reaction, it does not follow that it is an actual reaction intermediate. Tamaru [7] emphasized the importance of measuring adsorption during the reaction to identify the reaction intermediate from kinetic behaviour of the surface species. This dynamic method has been applied using the infra-red spectroscopic technique. Accordingly, not only the rate of the overall reaction but also the kinetic behaviour of the adsorbed species during the course of the reaction were measured as a function of their coverage, as was done in the decomposition of formic acid.[8]

EXPERIMENTAL

The catalysts were zinc and magnesium oxides. The zinc oxide was obtained from the New Jersey Zinc Co. and the magnesium oxide from Merck Co. Ltd. The surface area was 10 m^2/g and 89 m^2/g for ZnO and MgO (B.E.T. method) respectively. The apparatus consisted of two cells directly connected to a closed circulating system, one contains a disc of ZnO (*ca.* 0.3 g) to study the chemisorbed species on the catalyst [8] and the other a lot of discs (total weight *ca.* 11 g) to measure the rate of the overall reaction as well as the selectivity of decomposition of the surface adsorbed species. The coverage of the surface species during the reaction and their kinetic behaviour were measured by means of infra-red spectroscopy in the range 4000-900 cm^{-1}. The selectivity of the decomposition of the surface species and the rate of the overall reaction were measured by the gas chromatographic technique using a dioctyl sebacate column for carbon dioxide and a molecular sieve 13× for carbon monoxide and hydrogen. Carbon dioxide was obtained from the decomposition of $NaHCO_3$ and was purified by vacuum distillation. Carbon monoxide was prepared from concentrated sulphuric acid and sodium formate and was passed through a liquid-nitrogen trap.

RESULTS AND DISCUSSION

MECHANISM OF THE WATER-GAS SHIFT REACTION ON ZnO

A ZnO disc (about 300 mg) in the infra-red cell was treated in vacuum at 400°C for 5 h. Then the mixture of 100 mmHg of carbon dioxide and 100 mmHg of hydrogen was introduced to the catalyst and was heated at 200°C for 2 h. The infra-red spectra of adsorbed species on ZnO were observed after evacuation of the gas-phase mixture, these are given in fig. 1*a*. On the other hand, 0.7 mmHg of formic acid vapour was conducted at room temperature on to ZnO disc pretreated under the same conditions. A similar infra-red spectrum was obtained after removing the acid vapour (fig. 1*b*). Accordingly, the formation of surface formate ion on the catalyst was confirmed when a mixture of carbon dioxide and hydrogen was introduced over the catalyst. The bands at 2870, 1572 and 1369 cm^{-1} are assigned to the

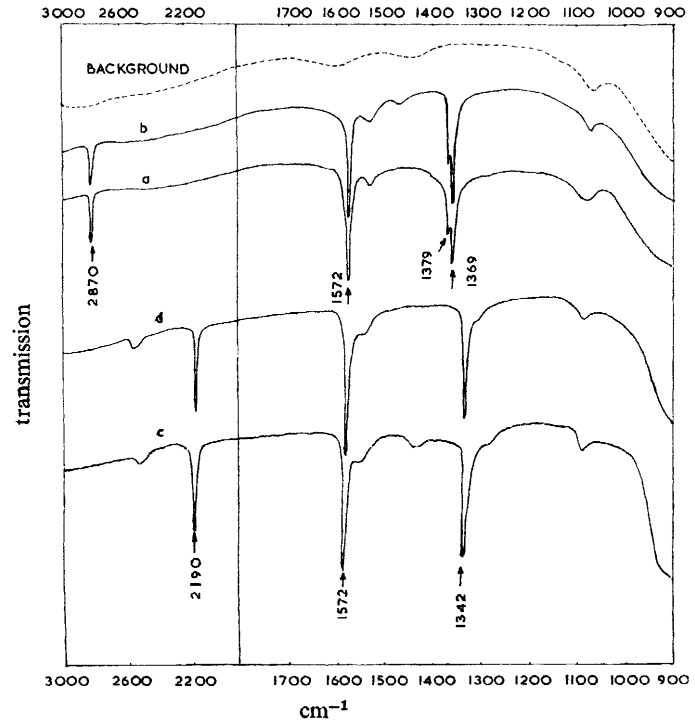


FIG. 1.—Infra-red spectra of the chemisorbed species on ZnO at 150°C. (*a*) CO_2 and H_2; (*b*) HCOOH; (*c*) CO_2 and D_2; (*d*) DCOOD.

C—H stretching, O—C—O antisymmetric stretching and O—C—O symmetric stretching vibrations, respectively, and the C—H inplane bending vibration band was found at 1379 cm^{-1}. The isotope shift of the C—H (and C—D) stretching vibration bands was observed employing deuterium gas or deuterated formic acid vapour (DCOOD), these are shown in fig. 1*c* and 1*d*. It was, however, difficult to detect the surface formate ion from the mixture of carbon monoxide and water vapour on ZnO at 200°C.

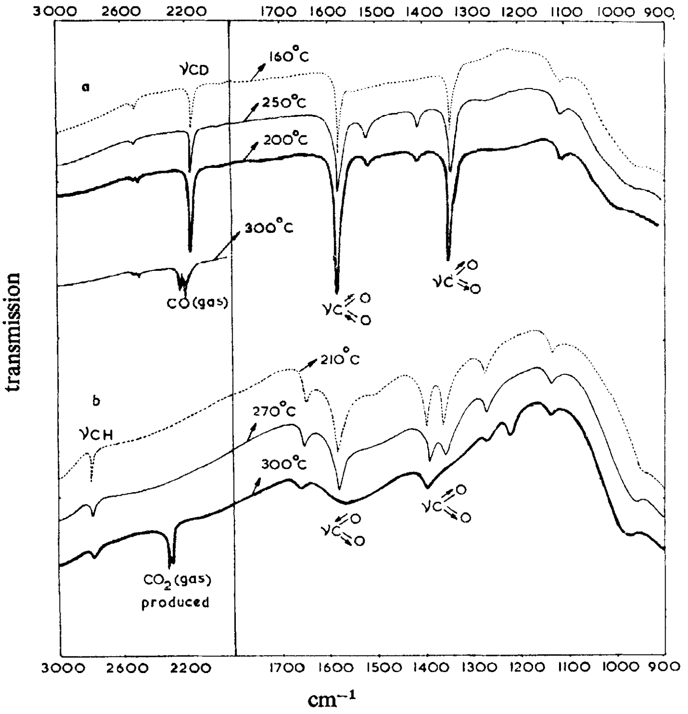


FIG. 2.—(*a*) Change in the infra-red spectra of the mixture of CO_2 and D_2 adsorbed on ZnO with temperature. (*b*) Change in the infra-red spectra of the mixture of CO and H_2O adsorbed on MgO with temperature.

The dynamic behaviour of the surface formate ion at various coverage and temperature was studied by means of infra-red spectroscopy (fig. 2*a*). It appeared that the formate ion on ZnO is stable at 200°C, but at 300°C carbon monoxide was formed at a considerable rate by the dehydration decomposition of the surface formate ion. The rate of this decomposition on ZnO was examined by means of infra-red spectroscopy in order to compare with the rate of the overall reaction at the reaction temperature (230°C). At first, a known amount of formic acid (DCOOD) was adsorbed on ZnO and the optical density of the C—D stretching vibration band was measured. This procedure was carried out for various amounts of DCOOD adsorbed on ZnO, which gave a relation between the coverage (calculated from the amounts of adsorbed DCOOD taking the size of the formate ion as 17 Å^2/molecule) and the optical density of the C—D stretching vibration band, as is shown in fig. 3*a*. The relation between the decomposition rate of the surface formate ion on ZnO and its coverage was also obtained in a similar manner, by following the decrease of the C—D stretching vibration band with time, which is given in fig. 3*b*. Consequently, the dependence of the decomposition rate of the surface formate ion upon its coverage could be obtained at the reaction temperature (230°C).

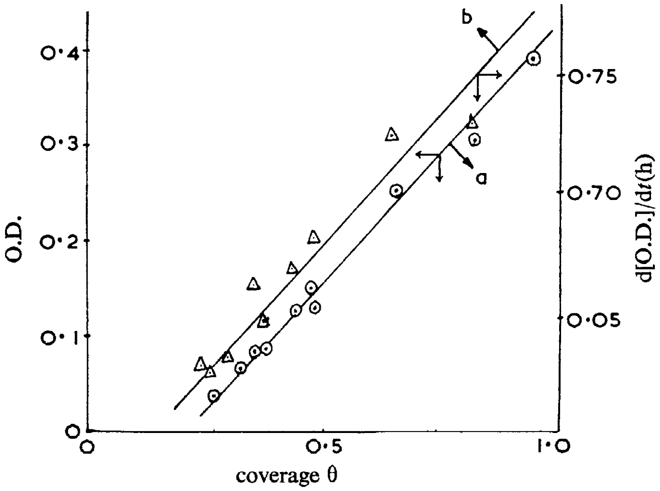


FIG. 3.—(*a*) Dependence of the optical density ([O.D.]) of ν_{C-D} upon the coverage (θ) of DCOO (*a*) on ZnO. (*b*) Dependence of the decomposition rate (d[O.D.]/d*t*) of surface formate upon its coverage θ on ZnO, by following the decrease of the C—D stretching vibration band with time.

The decomposition of the surface formate ion proceeds in two different manners; dehydration to form CO and dehydrogenation to CO_2. The selectivity of the decomposition was defined as the fraction of carbon monoxide in the total carbon monoxide and carbon dioxide produced, $CO/(CO+CO_2)$. The dependence of the selectivity upon the coverage at 230°C is given in fig. 4*a*. The rate of the dehydration decomposition of the surface formate ion was estimated by multiplying the rate of

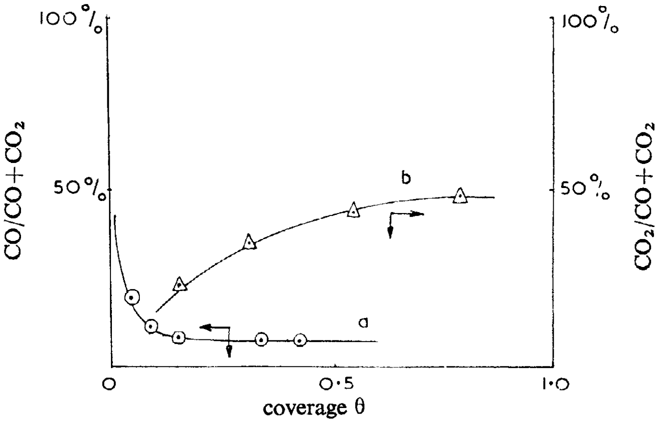


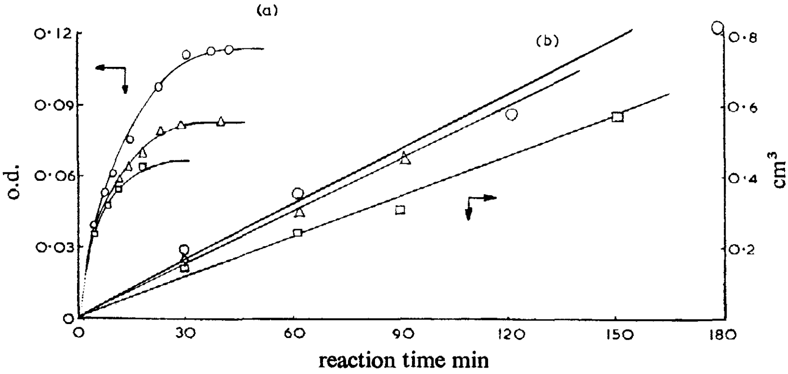
FIG. 4.—Selectivity of the decomposition of surface formate on the catalyst at various coverages: (*a*) on ZnO; (*b*) on MgO.

decomposition by the selectivity at the same coverage. On the other hand, the rate of the overall reaction and the coverage of surface formate were measured by the infra-red technique and gas chromatographic analysis of the amounts of carbon monoxide produced (fig. 5). The rate of dehydration decomposition of the surface formate ion on ZnO and that of the overall reaction were calculated from fig. 5

and are given in table 1 with the coverage of the formate ion on ZnO in the steady-state. Both rates were in reasonable agreement within the experimental error, which led to the conclusion that the surface formate ion is the real reaction intermediate of the water-gas shift reaction on ZnO. The mechanism is considered to be as follows:

$$\left.\begin{array}{l} H_2(g)\rightleftharpoons 2H(a) \\ CO_2(g)\rightleftharpoons CO_2(a) \end{array}\right\} \overset{1}{\rightleftharpoons} \begin{array}{c} HCOO(a) \\ H(a) \end{array} \overset{2}{\rightleftharpoons} \left\{\begin{array}{l} OH(a)\rightleftharpoons H_2O(g) \\ CO(a)\rightleftharpoons CO(g). \end{array}\right.$$

The dehydration step (2) is the rate-determining step of the reaction.



(a) ZnO=0.2755 g; (b) ZnO = 11.588 g

FIG. 5.—(a) Concentration of surface formate measured by the infra-red technique. (b) The rate of the overall reaction measured by the gas chromatographic analysis of the amounts of CO produced. □, CO_2 5.5 cmHg, D_2 5.5 cmHg; △, CO_2 10.5 cmHg, D_2 10.5 cmHg; ○, CO_2 16.0 cmHg, D_2 16.0 cmHg.

TABLE 1.—COMPARISON OF THE RATE OF THE DEHYDRATION OF SURFACE FORMATE WITH THAT OF THE OVERALL REACTION ON ZnO AT 230°C

	$D_2+CO_2\rightarrow D_2O+CO$	$D_2CO_2(a)\rightarrow D_2O+CO$	coverage of $DCO_2(a)$ (θ)
I	0.023 cm³/g h	0.022 cm³/g h	0.35
II	0.028	0.025	0.38
III	0.030	0.029	0.41

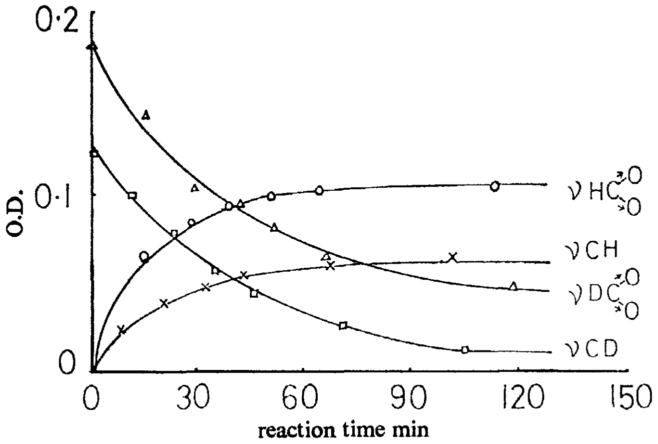


FIG. 6.—The rate of hydrogen exchange between DCOO (a) and H_2 on ZnO at 230°C.

In addition to these observations, it was also found by infra-red spectroscopy that the exchange reaction, $H_2+DCOO(a) \rightleftharpoons HD+HCOO(a)$, proceeded easily on the surface on the ZnO catalyst at the reaction temperature as is shown in fig. 6. The rate of decomposition of surface formate was not greatly influenced by the additional water adsorbed under the reaction conditions employed, (fig. 7). In this case 0.3 cm (s.t.p.) of H_2O vapour was added to 0.25 g of catalyst during the course of the decomposition of surface formate ions.

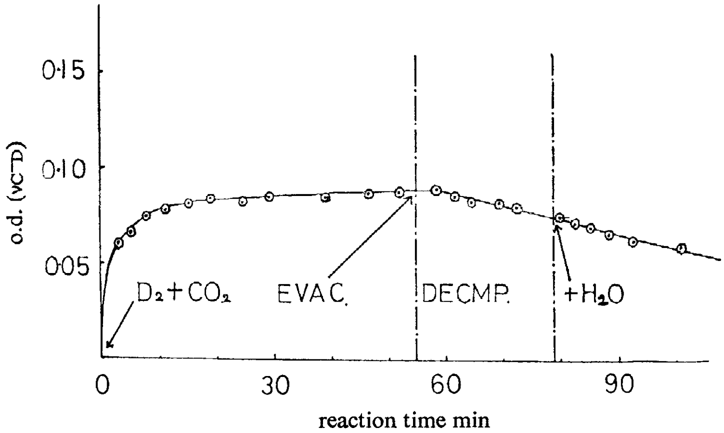


FIG. 7.—The influence of the additional water upon the rate of the decomposition of surface formate on ZnO.

MECHANISM OF THE WATER-GAS SHIFT REACTION ON MgO

When a mixture of 40 mmHg of carbon monoxide and 9 mmHg of water vapour was conducted onto a MgO disc (about 50 mg) treated in a vacuum at 400°C for 20 h, the formation of the surface formate ion on the catalyst was confirmed by means of infra-red spectroscopy, as had been found by Scholten (fig. 8*a*). A similar spectrum (fig. 8*b*) of adsorbed species was obtained when 0.7 mmHg of formic acid vapour was introduced on to the same disc at 150°C. The isotope shifts of the C—H (and C—D) stretching vibration band and the C—H (and C—D) inplane bending band were found by employing D_2O or DCOOD; these are shown in fig. 8*c* and 8*d*. It was, however, different from ZnO in that the surface formate ion could not easily be observed from a mixture of carbon dioxide and hydrogen. The change in the infra-red spectra of the formate ion on MgO with temperature was measured (fig. 2*b*). The formate ion on MgO was clearly observed at 210 and 270°C but at 300°C the reaction proceeded rapidly to form carbon dioxide by the decomposition of the surface species.

The relation between the coverage of the surface formate ion on MgO and the optical density of its C—H stretching vibration band, and the relation between the coverage and its decomposition rate at 280°C, was obtained in a similar manner as for ZnO by means of infra-red spectroscopy (fig. 9*a* and 9*b*). The selectivity was also measured at various coverages of the formate ion on MgO, but here it was defined as the ratio of the initial rate of carbon dioxide produced to that of the total carbon dioxide and carbon monoxide produced by the decomposition of the surface formate at 280°C (fig. 4*b*). The rate of the dehydrogenation decomposition of the surface formate ion was estimated by the same procedure as for ZnO, which was in reasonable agreement within experimental error with the rate of the overall reaction

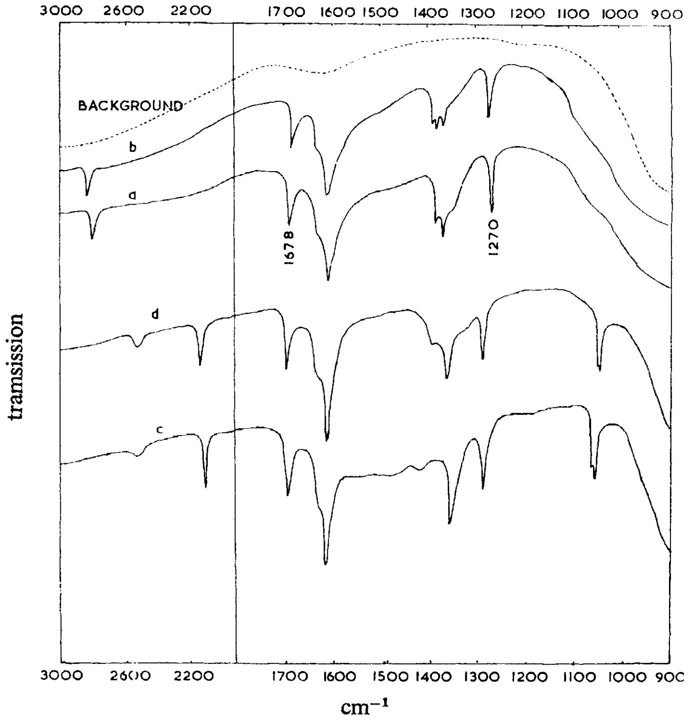


FIG. 8.—Infra-red spectra of the chemisorbed species on MgO at 150°C. (*a*) CO and H_2O; (*b*) HCOOH; (*c*) CO and D_2O; (*d*) DCOOD.

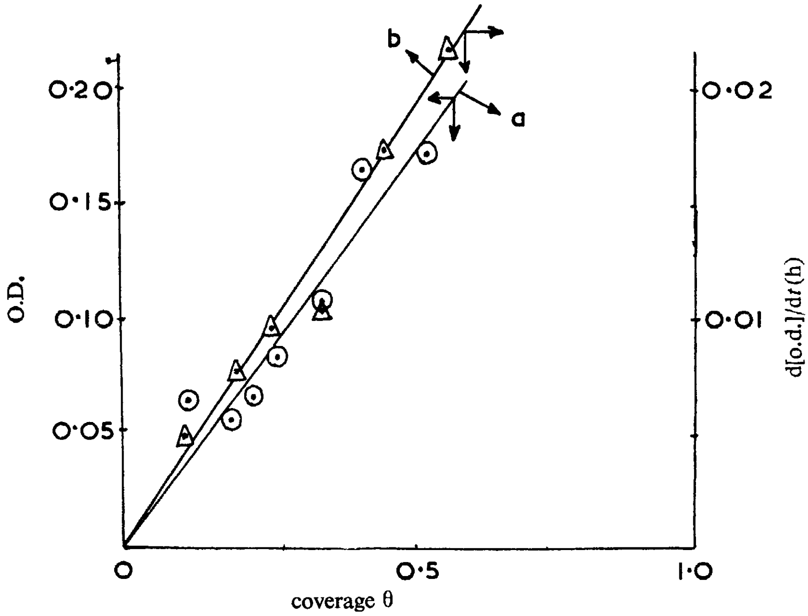


FIG. 9.—(*a*) Dependence of the optical density of ν_{C-H} upon the coverage of HCOO (*a*) on MgO (*b*) Dependence of the decomposition rate of surface formate upon its coverage on MgO.

on MgO which was obtained by gas chromatographic analysis for carbon dioxide produced as a function of reaction time (table 2). From these results, it was concluded that the surface formate ion is the reaction intermediate of the water-gas shift reaction on MgO. The rate-determining step is the dehydrogenation step (1) in the scheme described above.

TABLE 2.—COMPARISON OF THE RATE OF THE DEHYDROGENATION OF SURFACE FORMATE WITH THAT OF THE OVERALL REACTION ON MgO AT 280°C

	$H_2O+CO \rightarrow H_2+CO_2$	$H_2CO_2(a) \rightarrow H_2+CO_2$	coverage of $HCO_2(a)$ (θ)
I	0.011 cm^3/g h	0.017 cm^3/g h	0.06
II	0.023	0.025	0.07
III	0.031	0.037	0.08

The bands at 1678 and 1270 cm^{-1}, shown in fig. 8*a* and 8*b*, appeared only when carbon monoxide and water vapour were introduced over MgO. These bands did not shift when heavy water (D_2O) vapour was employed instead of H_2O. It is considered that these bands would be due to the surface CO_3^- ion.[9]

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