JOURNAL OF CATALYSIS **39**, 369–374 (1975)

The Surface Formation of Manganese(II) Formate During the Dehydration and Dehydrogenation of Formic Acid on Manganese(II) Oxide

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Received February 18, 1975

The decomposition of formic acid on manganese(II) oxide has been studied from 250 to 300°C in a flow system at atmospheric pressure. Both dehydration and dehydrogenation reactions occurred with formic acid partial pressures from 10 to 70 Torr. The activation energy, 32 ± 1 kcal $mole^{-1}$, and the preexponential factor, 4.7×10^{24} molecules cm^{-2} s^{-1}, for dehydration are in agreement with published data. An activation energy of 21 ± 1 kcal $mole^{-1}$ and preexponential factor of 7.4×10^{20} molecules cm^{-2} s^{-1} have been determined for the dehydrogenation reaction on this catalyst for the first time.

Direct structural confirmation for the formation of manganese(II) formate on the catalyst surface was obtained by X-ray diffraction and the relative amount formed was determined by thermogravimetric analysis. Scanning electron microscopy also showed significant changes in the catalyst texture with temperature increase from 200 to 350°C. The dehydrogenation selectivity of the catalyst decreases with increase in the reaction temperature and it is shown that this phenomena may be related to the amount of metal formate present.

INTRODUCTION

The catalytic decomposition of formic acid has been studied extensively on both metals and metal oxides. It may be considered as a model reaction in attempts to obtain correlations between catalyst activity and selectivity on the one hand and surface physical and chemical properties on the other. The literature has been reviewed quite recently (*1*).

The present communication describes a study of the decomposition of formic acid on manganese(II) oxide not only in conjunction with previous work on the general catalytic properties of this oxide (*2*) but also to obtain data on the possible surface formation and stability of formate-type species. Such species are believed to form as intermediates during the water–gas shift reaction on zinc(II) and magnesium(II) oxides (*3,4*), and although the shift reaction on manganese(II) oxide has been proposed to proceed via a redox mechanism (*5*), it was felt that further supporting data for the proposal might be obtained through a comparison of kinetic parameters for the shift and formic acid reactions on this oxide.

It may be noted also that apparently conflicting results have been reported for the selectivity of manganese(II) oxide in formic acid decomposition. Thus it has been shown that the oxide was exclusively active in dehydration (*6*) but complete selectivity for dehydrogenation has also been reported (*7*) in agreement with results on the mode of decomposition of the metal formate (*8*).

EXPERIMENTAL METHODS

The all-glass flow system and quartz reactor were slightly modified from that used previously (*5*). Teflon seals and stopcocks were incorporated throughout the system.

High-purity helium was used as the carrier gas at atmospheric pressure in the flow system and in the Beckman GC-5 gas chromatograph. Carbon monoxide, carbon dioxide, water and formic acid were analyzed by a thermal conductivity bridge using stainless steel columns, 120 × 0.125 in. o.d., packed with "Poropak Q" (120–150 mesh). The catalytic rates of reaction were evaluated by monitoring the amounts of carbon monoxide, carbon dioxide and water present in the effluent gases from the reactor.

The preparation of α-manganese(III) oxide (*2*) and subsequent conditioning (*5*) to prepare manganese(II) oxide have been reported. AnalaR formic acid (B.D.H. Ltd.) freshly distilled from anhydrous copper(II) sulfate was used in the helium-gas saturators which were degassed prior to use. Check measurements on the catalytic results were also completed using formic acid which had been previously purified to $>99\%$ by preparative chromatography in order to remove trace amounts of acetic acid.

Surface areas were measured by low temperature krypton adsorption (BET; $-196°C$; $\sigma = 21.5$ Å^2). Thermogravimetric weight-loss data were recorded on a Stanton-Redcroft Model HT5A thermobalance. After exposure to formic acid, approximately 300 mg of the catalyst was transferred to the thermobalance and flushed in nitrogen at 300 ml min^{-1} (NTP). Preliminary experiments using nickel powder established that a nitrogen gas flow rate of 100 ml min^{-1} (NTP) was sufficient to prevent diffusion of air into the heated zone of the thermobalance. Thus oxidation of manganese(II) oxide, formed from the formate decomposition, to manganese(III) oxide was avoided. The amount of manganese(II) formate present was then calculated from the thermogravimetric weight-loss curves obtained isothermally at 360°C in 300 ml min^{-1} nitrogen (NTP).

RESULTS

Preliminary experiments showed that above 325°C, formic acid decomposition on the reactor walls reached levels slightly greater than 1% and hence 300°C was kept as the highest temperature for the flow study. Reaction rate measurements at the various temperatures were made after the steady catalytic activity level had been established at 300°C after 2 hr with a formic acid partial pressure of 40 Torr. After the rate measurements had been completed the catalysts were allowed to cool to room temperature in a helium stream.

The Nature of the Surface

After exposure to the water–gas mixture catalysts were dark brown in color but on subsequent exposure to formic acid the color changed to blue at 250°C and to brown at 350°C.

X-Ray powder diffraction photographs of catalysts exposed to formic acid showed distinct lines characteristic of manganese(II) formate (*9*) as well as manganese(II) oxide. The ASTM *d* spacings (Å) for manganese(II) formate dihydrate include 4.65, 70%; 4.43, 50%; 3.40, 30%; 3.09, 20%; 2.81, 10%; and 2.20, 12% (found: 4.65, 75%; 4.40, 60%; 3.41, 25%; 3.09, 25%; 2.81, 10%; and 2.25, 10%).

Electron micrographs of the oxide before and after exposure to formic acid showed that significant changes had occurred in particle geometry. Thus transmission micrographs (microscope magnification ×26,000) of samples before exposure were characterized by crystallites of approximately 700 Å diameter coalesced into particles averaging 0.05 mm diameter. After exposure, the transmission micrographs of the samples were characterized by the presence of highly agglom-

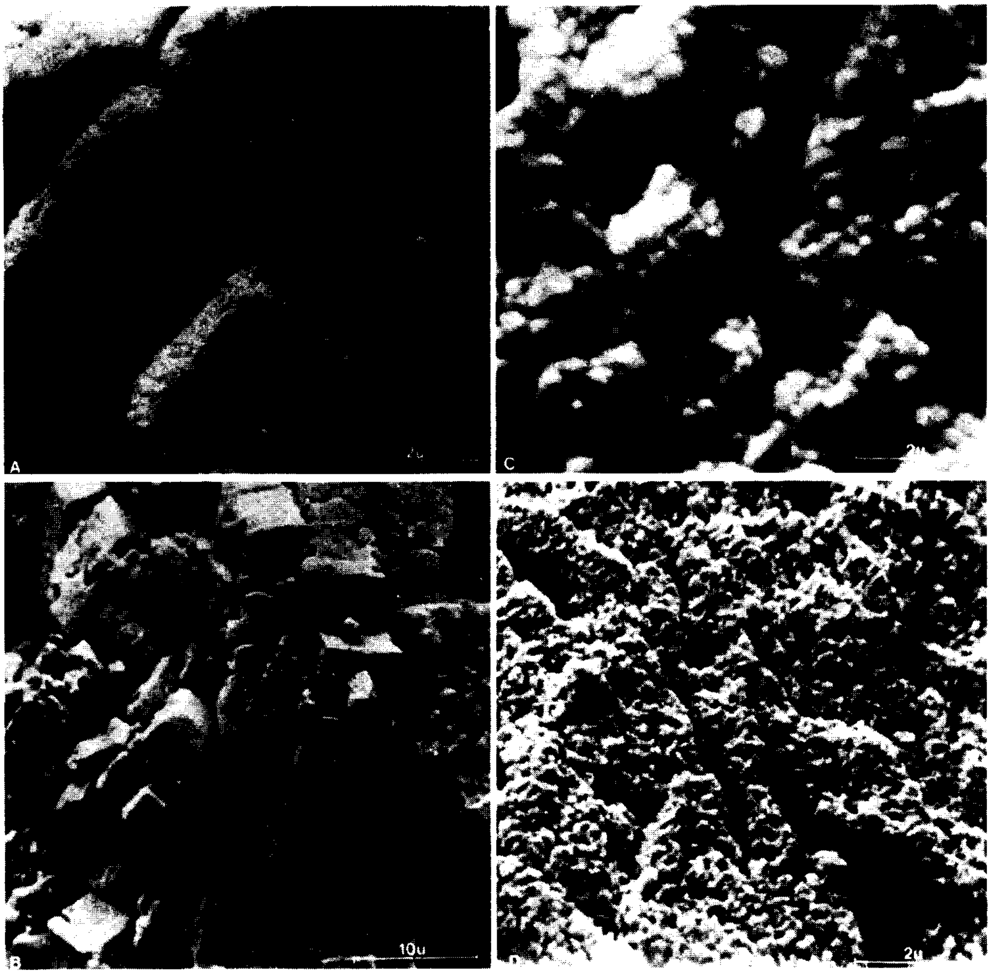

FIG. 1. Scanning electron micrographs of manganese(II) oxide after exposure to formic acid for 2 hr at: 200°C (A and B); 275°C (C); and 325°C (D). Magnification factors for (A, C, and D) 23,000×; and for (B) 4600×.

erated particles which appeared to be opaque in the electron beam. Carbon–platinum replicas also showed clearly that considerable agglomeration had occurred.

Scanning electron micrographs are reproduced in Fig. 1 which shows the presence at 200°C of a separate crystalline phase (Fig. 1A and B). Spherical aggregates occur at 275°C, C. At 325°C, D, the electron photomicrographs appeared identical to those obtained with samples of manganese(II) oxide before exposure to formic acid.

Table 1 and Fig. 4 show the fraction of manganese(II) formate formed as calculated from thermogravimetric weight-loss curves. From 200 to ~250°C, the amount of formate increased from 59 to 68% and decreased to ~1% at 350°C. The specific surface area of the catalyst samples did not change significantly from 250 to 300°C and was taken to be 14 $m^2 g^{-1}$.

Reaction Rate Order with Respect to Formic Acid Partial Pressure

Rate orders were determined at 250 and 300°C in the partial pressure range 10–70 Torr, Fig. 2. The rate of decomposition was independent of formic acid partial pressure from ~20 to 70 Torr at 250°C

TABLE 1

THE EFFECT OF TEMPERATURE ON THE RATES OF DEHYDRATION AND DEHYDROGENATION AND ON THE FRACTION OF MANGANESE(II) FORMATE PRESENT[a]

Temp (°C)	Rate of reaction × 10^9 (molecules m^{-2} s^{-1})		Dehydration selectivity $[r_1/(r_1 + r_2)]$	Fraction of manganese(II) formate present
	Dehydration (r_1)	Dehydrogenation (r_2)		
350	—	—	—	0.007
325	—	—	—	0.037
300	49.0	120.0	0.290	0.405
290	26.9	87.1	0.236	—
280	14.1	66.1	0.213	—
275	—	—	—	0.535
270	6.9	45.7	0.132	—
260	4.2	32.0	0.115	—
250	2.2	26.9	0.074	0.690
225	—	—	—	0.659
200	—	—	—	0.590

[a] Partial pressure of formic acid = 40 Torr.

and from ~30 to 70 Torr at 300°C. Below these regions the rate increased with decrease in partial pressure. Thus, for the range of partial pressures studied later, a zero order kinetic expression was used to calculated rate constants in accord with results reported elsewhere (*6,11*) for this catalyst.

Temperature and Selectivity Effects

The rate of reaction was determined from 250 to 300°C at 10°C intervals and rate constants were calculated. The Arrhenius plots of these constants are shown in Fig. 3. The activation energy and preexponential factor for the dehydrogenation reaction, curve A, were 21 ± 1 kcal $mole^{-1}$ and 7.4 × 10^{20} molecules cm^{-2} s^{-1}, respectively. For dehydration, curve B, these values were 32 ± 1 kcal $mole^{-1}$ and 4.7 × 10^{24} molecules cm^{-2} s^{-1}, respectively. The Arrhenius parameters for the dehydration reaction correspond closely with previous results (*6*).

The reaction rate and dehydration selectivity values are presented in Table 1. Figure 4 shows the pattern of increase in the

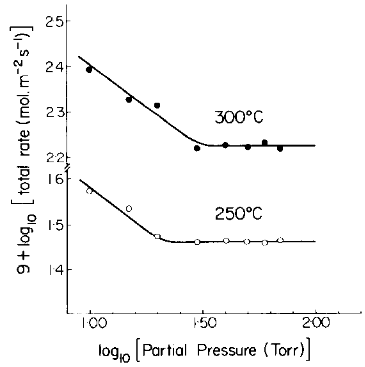

FIG. 2. The effects of variations in formic acid partial pressure on the reaction rates at 250 and 300°C.

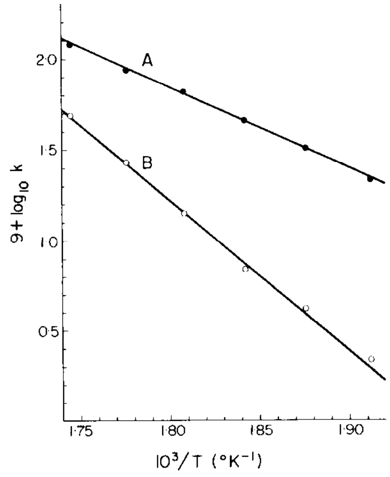

FIG. 3. Arrhenius plots of the reaction rate constant, *k*, for the dehydrogenation (A) and the dehydration (B) of formic acid on manganese(II) oxide from 250 to 300°C.

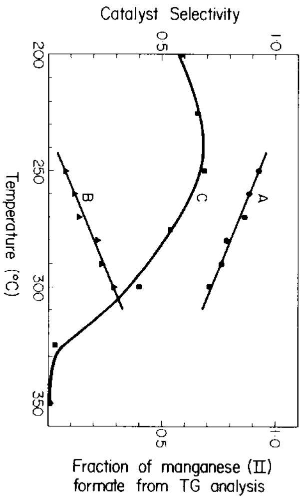

FIG. 4. Selectivity of manganese(II) oxide toward dehydrogenation (A) and dehydration (B) in the temperature range 250 to 300°C. Curve C represents the fraction of manganese(II) formate present after catalysis in the temperature range 200–350°C.

dehydration selectivity from 250 to 300°C while the selectivity for dehydrogenation decreases correspondingly.

DISCUSSION

Direct evidence has been obtained for the formation of manganese(II) formate on the surface of manganese(II) oxide during formic acid decomposition. The formate was not so detected in studies of the water–gas shift reaction on the same oxide (*5*) but this observation alone would not exclude the possibility of its formation as a transient intermediate. However, comparisons of rate constants and activation energies for the two reactions yield clear evidence that the formation of manganese(II) formate is at least unlikely to be a rate-determining step in the water–gas shift reaction on manganese(II) oxide. Thus, while the activation energies for the dehydration and dehydrogenation of formic acid are 32 ± 1 and 21 ± 1 kcal mole^{-1}, respectively, the value for the water–gas shift reaction was 11 ± 0.5 kcal mole^{-1} at similar temperatures on the same catalyst preparation.

Formaldehyde was not detected in the products of catalysis in this study and hence the overall reactions to be considered are:

$$\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2, \qquad (1)$$

$$\text{and HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}. \qquad (2)$$

Elsewhere, the decomposition on this oxide has been reported to yield dehydrogenation products exclusively, in accord with the products obtained during the thermal decomposition of manganese(II) formate at 338°C (*8*) and 300°C (*7*). However, it has been suggested that the presence of metallic manganese in these solids may have had considerable influence on the selectivity (*11*). From published thermodynamic data (*12*), dehydrogenation would be expected to be slightly more favored than dehydration from 25 to ~700°C. Nevertheless the contribution of the dehydration reaction to catalysis is significant for this catalyst at 300°C becoming progressively less so as the temperature was decreased to 250°C where the selectivity for dehydration was 0.074.

The thermogravimetric data indicate that between 250 and 350°C, the large amounts of manganese(II) formate produced during the decomposition of formic acid appear to be related to the selectivity for dehydrogenation since both of these parameters decreased coincidentally with temperature. Thermal decomposition studies (*13*) on bulk manganese(II) formate in the same temperature range indicate that the formate decomposes predominantly via dehydrogenation at α, fraction decomposed, > 0.2. This also suggests that the observed catalytic selectivity may be influenced by the presence of a manganese(II) formate phase. Consequently a decrease in selectivity towards dehydrogenation would be expected to occur as the amount of formate formed decreases which is consistent with the results shown in Fig. 4.

Extrapolation of the selectivity data suggests that the catalyst would exhibit similar selectivity values for dehydrogenation and dehydration at around 350°C while above this temperature the dehydration reaction should become predominant. There would then be a minimal amount of manganese(II) formate present and its formation would be limited to the surface of the oxide probably as a transient species: the decomposition of which would not be influenced by the same lattice constraints that are present during the decomposition of the bulk material.

Thus, the selectivity of manganese(II) oxide in formic acid catalysis between 250 and 300°C appears to be distinctly related to the presence of a separate manganese(II) formate phase which decomposes predominantly via a dehydrogenation reaction in which rate control may be associated with the loss of stability of the formate intermediate, as has been proposed previously (*6*). The increase in dehydration selectivity with temperature could then be related to an increasing proportion of manganese(II) oxide on the catalyst surface on which sites the formic acid decomposes rapidly via reaction (*2*). Previous studies have indicated that this reaction may also proceed through a transient formate intermediate (*1*)—its formation and subsequent decomposition being much more rapid than it is in the dehydrogenation process.

The observed change in the reaction rate with respect to formic acid partial pressure between 10 and about 30 Torr at 250 and 300°C, Fig. 2, is believed to be associated simply with an equilibration process involving formic acid vapor and the oxide catalyst. Thus, with increasing formic acid partial pressure, the amount of manganese(II) formate present would be expected to increase and thereby limit proportionally the formate decomposition to that associated with the solid phase. This kinetic region would correspond to the nucleation and growth of the surface formate and its subsequent penetration, through reaction, into the bulk of the oxide.

ACKNOWLEDGMENTS

We thank Mr. A. T. MacKenzie and Mr. S. Spivak for expert technical assistance.

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