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Mechanism of Formic Acid Decomposition on 3*d* Metal Oxides

J. M. CRIADO, F. GONZALEZ, AND J. M. TRILLO

Departamento de Quimica Inorganica, Universidad de Sevilla, Seville, Spain

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A study has been made of factors pertaining to the selectivity of 3*d* metal oxides in the catalytic decomposition of formic acid. Oxides of all the 3*d* metals have been prepared and their activity was measured in the formic acid reaction. For the purpose of a more general discussion, results from earlier papers also are used.

The comparison of the activation energy of formic acid decomposition on TiO_2, V_2O_3, Cr_2O_3, MnO, and Fe_3O_4 with that of the decomposition of the corresponding formates supports the view that the formate intervenes in the decomposition reaction mechanism of formic acid on these oxides in the two main reactions of dehydrogenation and dehydration.

The rate determining step of the dehydrogenation reaction seems to consist of the loss of stability of the intermediate formate through the transfer of electrons to the catalyst. The experimental results indicate that the dehydration of formic acid on 3*d* oxides takes place through two different mechanisms, one in which the rate determining step is the elimination of water from two surface OH groups, in the cases of TiO_2, V_2O_3, and Cr_2O_3, and another in which the reaction rate is determined by the breaking up of the C–O bond of the formate, in the cases of Fe_3O_4 and MnO.

I. INTRODUCTION

The catalytic decomposition of formic acid on metals and metal oxides constitutes one of the reactions which has provided most information about the formation and stability of surface intermediates. By infrared spectroscopy (*1*, *2*) the presence of formate has been noticed in metals and metal oxides, except very acidic oxides such as silica (*3*, *4*). In a great number of cases a correlation has been found between the decomposition temperature of the formates and the activation energy for the catalytic decomposition of formic acid on the corresponding metals or oxides (*5*). However, due to the influence exercised by the preparation and pretreatment of the sample, both on the catalytic activity of oxides and on the thermal stability of the salts, the results published as yet have not been very accurate.

In the present study of the catalytic activity of 3*d* metal oxides, in which we complete our results (*6*) on chromium and titanium oxides, the activation energy of these oxides for the decomposition reaction of formic acid is related to that of decomposition of the corresponding formates, these latter having been obtained in the form of a thin layer on the surface of the oxides. Thus a quantitative relationship has been found between both magnitudes, contrary to the results published up to the present moment.

Although it had been established that the general mechanism of decomposition of formic acid on 3*d* metal oxides consisted of the adsorption of the molecule followed by the decomposition of the surface formate and by the desorption of the reaction products (*7*), the details of evolution of this formate species in relation to the selectivity of the oxide are not known. On attempting to relate the selectivity to some properties of the solids, such as the electronic factor, some apparent contradictions emerge in the papers of different authors.

In the present paper, mechanisms for the dehydrogenation and dehydration reactions are put forward, which are in agreement with our results and those of other authors. The sequence followed by the catalytic selectivity in the oxide series is related to the variation of the interaction of the surface formate with the solid.

II. Experimental Methods

A Schwab-type dynamic differential reactor (*8*) modified by us, has been used to measure the activity of the catalysts. The liquid formic acid flows to an evaporator from a system of capillaries which allows a series of constant flows to be obtained. The acid, once it has been evaporated, passes through the reactor in which the catalyst lies, spread out finely on a sheet of porous glass.

The water formed in the decomposition of the acid, and the acid which has not reacted, are collected in a condensor installed at the mouth of the reactor. The total flow of CO, CO_2, and H_2 gases produced is measured in a connected analysis system formed by two gas gauges and a CO_2 intermediate adsorption column.

Schuchard formic acid 100% for chromatography was used.

III. Results

Catalysts. V_2O_5 has been prepared by decomposing the hydrated oxide at 500°C in air, after having precipitated it in a solution of NH_4VO_3 at 50% with Riedel nitric acid at 65%.

Mn_3O_4 and Fe_3O_4 have been obtained by precipitating their hydroxides with ammonia from the corresponding nitrate solutions (Merck r.a.), afterwards washing the precipitate with boiling water to eliminate the nitrates and drying it at 110°C. $Mn(OH)_2$ decomposed at 1100°C over a period of 40 hr in an air atmosphere, and $Fe_2O_3 \cdot nH_2O$ after 5 hr in a hydrogen stream at 400°C.

CoO and NiO were prepared by calcination of their nitrates. $Co(NO_3)_2 \cdot 9H_2O$ (Merck r.a.) was heated for 5 hr at 1000°C in air and cooled in nitrogen; $Ni(NO_3)_2 \cdot 9H_2O$ (Merck r.a.) was heated in air for 10 hr at 500°C.

Once the catalysts were prepared, they were ground and sieved, and the fraction which passed through a 23 A. F. N. O. R. sieve (0.16-mm mesh) was collected. Before and after treatment with formic acid vapor at reaction temperature, catalysts were characterized by chemical analysis, X-rays and specific surface measurement by the BET method. The results obtained are shown in Table 1. We have also included in this table, and will continue doing so throughout the paper, the titanium and chromium oxides studied previously (9) to facilitate a better understanding of the general considerations.

It can be observed that the vanadium, manganese, cobalt, and nickel suffer a reduction, the iron oxide oxidizes in part and the titanium and chromium oxides remain unchanged. When we refer to the catalytic activity we shall use the denomination of the phases referred to in the third column of Table 1, as they are the truly active ones in the catalytic reaction.

The Fe_3O_4 sample oxidizes partially to γ-Fe_2O_3 in contact with formic acid vapor, but it should be noted that the sample which was used to carry out the X-ray study and the chemical analysis has been obtained in somewhat different conditions to those which exist in the reactor when the catalytic activity of the magnetite is measured.

TABLE 1
Catalysts

Original sample	Specific surface ($m^2\ g^{-1}$)	Sample treated with HCOOH at 400°C	Specific surface ($m^2\ g^{-1}$)
TiO_2	4.2	TiO_2	4.2
V_2O_5	1.3	V_2O_3	18.8
Cr_2O_3	8.9	Cr_2O_3	8.9
Mn_3O_4	1.3	MnO	6.0
Fe_3O_4	13.1	$Fe_3O_4 + \gamma$-Fe_2O_3	13.1
CoO	0.1	α,cubic-Co	10.0
NiO	7.4	Ni	2.0

A very fine layer of catalyst was used to measure the catalytic activity, while in the preparation of the sample treated with formic acid for its textural and analytical study, the sample bed was considerably larger; the resistance which the bed exercises on the diffusion of the formic acid and of the decomposition products is very important in this case.

It is to be expected that in the latter conditions the partial pressure of steam in contact with the sample will be much greater, thus favoring the oxidation, since, as is known steam exercises a catalytic effect on the oxidation reaction. For this reason, we shall consider that the active phase of iron oxide in the decomposition reaction of formic acid is Fe_3O_4.

Catalytic activity. The catalytic activity of the formic acid decomposition reactions has been measured between 400 and 470°C at such short contact times that the reaction rate was independent of contact time. The possible occurrence of the water–gas reaction does therefore not obscure the selectivity. The kinetic conditions are zero-order.

The formation of formaldehyde has been investigated by analysis with chromotropic acid (*10*). It has been found that the relative proportion of acid which decomposes in the direction on MnO, the most active for this reaction, is less than 8%. In the remaining catalysts the proportion is lower than 1%. Consequently, only the full dehydrogenation to CO_2 and the dehydration reactions of the formic acid are taken into account. The values of the activation energies and frequency factors for both reactions on the different catalytst are shown in Table 2. When the activity for a reaction is not included, this means that its value is less than the precision of the experimental method.

The results in Table 2 show that MnO is only active in the dehydration reaction of formic acid, whereas cobalt and nickel are active exclusively in the dehydrogenation reaction.

However, the results in the literature on the catalytic activity of MnO for the decomposition of formic acid and of ethanol show that this oxide is active for both dehydration and dehydrogenation reactions, its selectivity towards the later being much higher. Thus, Eucken and Heuer (*11*), studying the decomposition of the ethanol on MnO, has observed that a partial reduction of the oxide to manganese metal is produced, the selectivity for the dehydrogenation changing from 67%, for pure oxide, to 95% when an incipient reduction is produced. This demonstrates the importance of the degree of surface oxidation of the oxide in its catalytic activity. Komarov *et al.* (*12*), studying the activity of the same oxide for the decomposition of formic acid, finds it is almost exclusively dehydrogenating, which agrees with the results which he obtained for the decomposition of $Mn(HCOO)_2$. Kornienko (*13*), too, reaches the conclusion that this salt decomposes according to a dehydrogenation, leaving a solid residue formed by 90% MnO and 10% manganese.

The fact that these results for manganese oxide do not coincide with our own may be due to the fact that the active centers

TABLE 2
FORMIC ACID DECOMPOSITION

Catalysts	E_{H_2} (kcal/mole)	A_{H_2} (molec/cm² · sec)	E_{H_2O} (kcal/mole)	A_{H_2O} (molec/cm² · sec)
TiO_2	46.5	4.7×10^{29}	25.0	1.9×10^{23}
V_2O_3	35.0	4.4×10^{25}	19.5	8.9×10^{20}
Cr_2O_3	37.0	6.0×10^{26}	17.0	2.8×10^{20}
MnO	—	—	33.0	9.0×10^{24}
Fe_3O_4	30.0	4.4×10^{24}	28.3	2.2×10^{22}
Co	11.0	8.3×10^{18}	—	—
Ni	24.2	4.6×10^{22}	—	—

which act in the dehydrogenation may have been poisoned by adsorption of the formaldehyde produced, or to the fact that the sample we prepared possesses a higher degree of surface-oxidation than those used by Eucken and Kornienko, since we have not observed the reduction to manganese metal.

As far as the catalytic activity of cobalt and nickel is concerned, practically all the studies which have been made indicate that they favor exclusively the dehydrogenation reaction of formic acid (*14*).

The rest of the catalysts are active in the two main reactions of decomposition of formic acid. If the activation energies given in Table 2 are compared with the decomposition ones of the corresponding formates, included in (*15*), we can observe that the activation energy values for the dehydration reaction of formic acid on TiO_2, V_2O_3, Cr_2O_3, and MnO, and for the dehydrogenation reaction of the same acid on Fe_3O_4, coincide with the decomposition of the formates. The fact that the analogy is established with only one of the two reactions according to which the formic acid decomposes can be explained, since in the intervals of temperatures at which the decomposition of the formates has been studied, the reaction mentioned above predominates in each case.

The activation energy values for formic acid decomposition on cobalt and nickel, however, disagree considerably with those which correspond to formates; this shows that on these metals the decomposition of the acid, in the range of temperatures used, does not occur through the same mechanism.

This is in agreement with the results in the literature on the decomposition of formic acid on nickel. As can be deduced from the results of Eischens and Pliskin (*16*) and from the data collected by Leftin and Hobson (*17*), at temperatures below 150–200°C, formic acid vapor decomposes on nickel through intermediate formate. The activation energy for the decomposition is between 22.7 and 24 kcal/mole. However, at temperatures above 200°C, this decomposition takes place through a different mechanism. According to Eischens and Pliskin, at these temperatures, the formic acid adsorbs covalently on nickel, decomposing later on.

On the other hand, Fukuda and colleagues (*18*) confirm these conclusions, establishing that the acid decomposition at low pressures on NiO is carried out simultaneously through two mechanisms, one through formate and another in which the formic acid interacts directly with the surface of the oxide, increasing the proportion in which this is produced with the temperature.

As for the decomposition of formic acid on cobalt, even though we do not possess confirmatory data, it should take place with an analogous mechanism to that in the case of nickel, in view of the great similarity which exists between the two metals.

IV. DISCUSSION

The value of the reaction rate at a given temperature (*19*), or the temperature at which the reaction rate reaches a fixed value (*20*), have been used so often to compare the catalytic activity of a series of catalysts that the validity of the correlations found between them and some properties of the catalysts is regarded as axiomatic. However, very different sequences for the catalytic activity may be obtained if one uses, for instance, a temperature different to that chosen by the authors (*21*). This may be understood if one has in mind the possibility of the simultaneous change of the activiation energy and frequency factor. For this reason the magnitudes of both quantities will be used in the present discussion.

In our preliminary work (*9*, *22*) on formic acid decomposition on titanium and chromium oxides it was shown by infrared spectroscopy studies that formate occurred as an intermediate. The comparison mentioned of the activation energy for the heterogeneous reaction of the decomposition of formic acid with that of the decomposition of the formates of titanium, vanadium, chromium, manganese, and iron, also support the idea that the formate intervenes in the decomposition reaction mechanism of formic acid on these *3d* mental oxides in the two main reactions of dehydrogenation and dehydration.

From the conclusions arrived at in previous work on the effect of doping (*23*, *24*), sintering temperature (*9*), treatment with diborane (*22*), and other, in addition to the above considerations, it can be deduced that although in the samples on the whole the decomposition reaction of formic acid takes place through an intermediate formate, the way in which this evolves depends on the sites in which the molecules of formic acid are chemically adsorbed. These sites are of a different nature for the two possible reactions of dehydrogenation and dehydration of the formic acid, thus allowing us to consider them separately as below.

Dehydrogenation reaction of formic acid. In the decomposition on Cr_2O_3 and TiO_2 via formate intermediate, we have also shown that the decomposition of this ion, according to the dehydrogenation reaction, is accompanied by the transfer of electrons from the adsorbate to the solid. This indicates that the rate determining step of the reaction should consist of the loss of stability of the intermediate formate through the transfer of electrons, as occurs in the homogeneous gas phase oxidation of formic acid with metals.

Again, the fact that in the other 3*d* oxides the decomposition of the acid also takes place through an intermediate formate, as well as the existence of a compensation effect between the activation energy for the dehydrogenation reaction and the logarithm of the frequency factor of all the oxides, including pure and doped chromium and titanium (Fig. 1) suggests that the reatcion is carried out on all of them through the same mechanism.

If we bear in mind that for titanium (*25*) and iron (*15*) oxides we have established the existence of 10^{14} active centers/per cm^2 for the formic acid dehydrogenation reaction, we reach the conclusion that the compensating effect present in them is due to a linear relationship between the activation energy and the entropy variation. In the other oxides, for which it has not been possible to determine the number of active centers, the effect may be due to the same cause, or to a simultaneous variation of the number of centers and the entropy factor; in any case, the mobility of the adsorbed phase with respect to the activated complex decreases as we descend the compensation line.

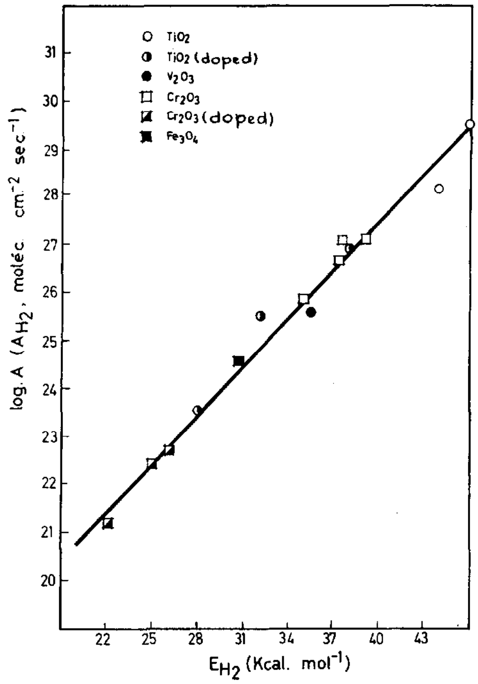


FIG. 1. Compensation effect of 3*d* oxides for the formic acid dehydrogenation reaction.

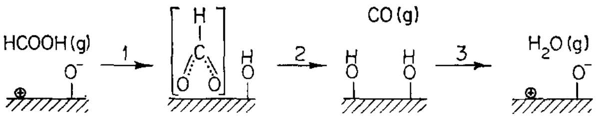
If the dehydrogenation of the formic acid takes place on all the 3*d* oxides through the suggested mechanism, a relationship should exist between the activation energy for the dehydrogenation reaction and the metal–formate bond energy. As a comparative measure of the values of this bond energy along the series can be taken the difference, ΔH, between the formation heats of the formate and the respective oxide. From the equation used by Fahrenfort (*26*) to calculate the formation heats of metal formates, a linear relationship between ΔH and formation heats of oxides can be deduced. In fact, we observe a linear relationship which extends to the oxides of titanium, vanadium, chromium, and iron, as shown in Fig. 2, in which we have plotted the activation energy for the formic acid dehydrogenation reaction against the formation heat of the oxides. This confirms that the breaking up of the metal–oxygen bond of the intermediate formate occurs in the rate determining step of the reaction, and consequently supports the proposed mechanism.

The fact that the series of doped titanium and chromium oxides is considerably removed from the straight line in Fig. 2 is due to the fact that the doping alters the stability of the surface oxygen of the oxide.

Dehydration reaction. As established above, the dehydration reaction on titanium, vanadium, chromium, manganese, and iron oxides takes place through an intermediate formate.

In some previous work in which we studied the effect of the sintering temperature of chromium and titanium oxides on their catalytic activity towards the decomposition of formic acid (*9*), was established that the Arrhenius preexponential factor of the dehydration reaction on these oxides increases in the same way as the amount of the adsorbed water on the samples. The activation energy, on the other hand, does not change. Moreover, in the case of TiO_2, Munuera (*27*) has established by means of studies on programmed thermal desorption that the energy and entropy of activation for (a) the dehydration reaction of formic acid and (b) water desorption at a high temperature possess identical values. This proves that the rate determining step of the dehydration reaction of the acid on these oxides is the desorption of water from surface OH groups.

These facts allow us to formulate for the dehydration of formic acid on titanium and chromium oxides the following mechanism as the most probable:



The rate determing step is 3, the active centers being Lewis acid sites generated from Brönsted centers by a mechanism analogous with that of Trambouze and coworkers (*28*).

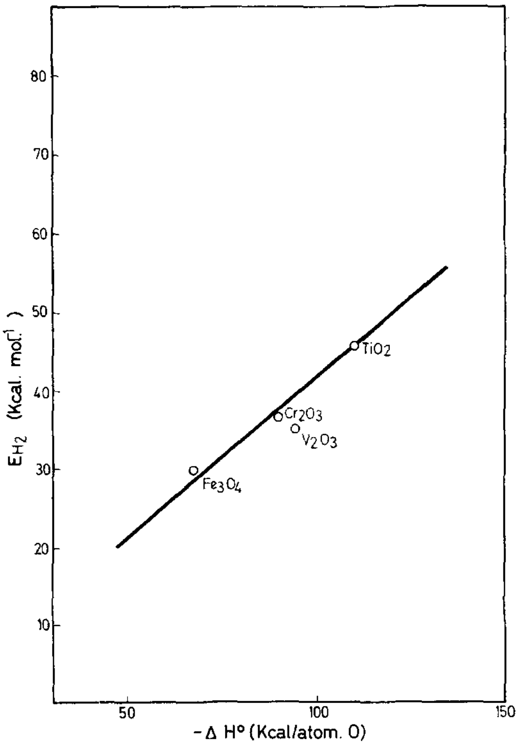


FIG. 2. Relationship between formation heat of 3*d* oxides and activation energy for formic acid dehydrogenation.

The experimental results included in Table 2 show that the activation energy for formic acid dehydration decreases throughout the series of 3*d* mental oxides until a minimum value is reached for Cr_2O_3, increasing abruptly on passing to the following oxides. Furthermore, the frequency factors per active site, calculated as in (*14*), are of the order of 10^8 sec^{-1} for the oxides of titanium, vanadium, and chromium, rising to 10^{10} sec^{-1} on passing to MnO.

These facts allow us to conclude that, in the case of V_2O_3, the rate determining step is the same as in TiO_2 and Cr_2O_3. The inhibition observed in the dehydration reaction of formic acid on TiO_2, V_2O_3, and Cr_2O_3, when the acid is water-diluted, agrees with above mechanism.

The sequence of the activation energies can be explained if it is borne in mind that the surface OH groups act as σ–π donors, and that the possibility of forming π bonds in these oxides becomes greater as the number of *d* electrons of the cation decreases, as that of the M–OH bond energy will decrease in the sense: TiO_2, V_2O_3, Cr_2O_3. As the electronic density in the metal–oxygen bond diminishes, so it increases in the hydrogen–oxygen bond; it follows then that the surface of the catalyst become more basic. Summing up, on passing from titanium oxide to chromium oxide in the series, the M–OH bond weakens and the MO–H bond becomes stronger. The elimination of a molecule of water between two neighboring surface hydroxyl groups will be carried out on each occasion with a lesser activation energy, giving a minimum for Cr_2O_3.

The formic acid dehydration seems to take place through a different mechanism on MnO and Fe_3O_4. In these oxides as the number of *d* electrons of the cation increases, the strength of the M–OH bond decreases. At the same time the stability of formate is increased, as a result of which the rate determining step of the reaction should now be the decomposition of the aforesaid formate, designated [2] in the general scheme described above.

The difference in activation energy for the MnO and Fe_3O_4 may have to do with the greater polarizing power of Fe(III) in comparison with Mn(II), which gives rise to the weakening of the C–O bond is the first case.

In Fig. 3, in which we have represented the activation energy of the oxides for the dehydration reaction of formic acid against the formation heat of the oxides a linear relationship can be seen for the oxides of titanium, vanadium, and chromium. This could be related to the change proposed in the rate determing step of the reaction.

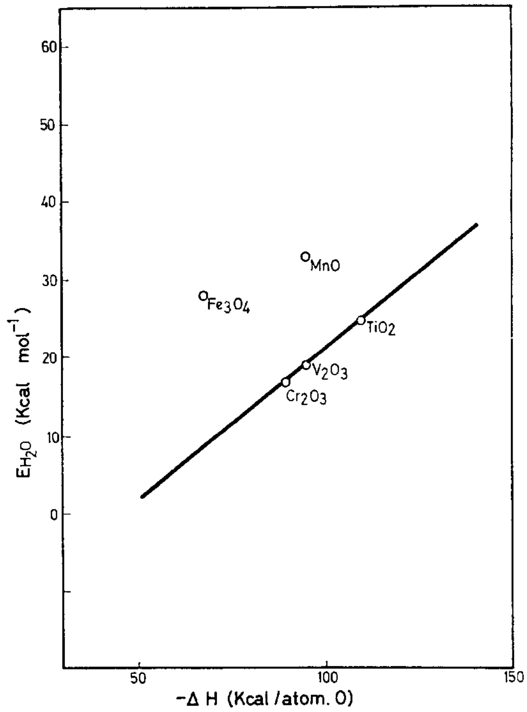


FIG. 3. Relationship between formation heat of 3*d* oxides and activation energy for dehydration of formic acid.

All the considerations which have been made show that the dehydration of formic acid on 3*d* oxides takes place through two different mechanisms; (i) in which the rate determining step is the elimination of water from two surface OH groups, which takes place on TiO_2, V_2O_3, and Cr_2O_3, and (ii) in which the dehydration rate is determined by the breaking-up of the C–O bond of the formate ion, which occurs on Fe_3O_4 and MnO.

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