JOURNAL OF CATALYSIS **168,** 255–264 (1997)
ARTICLE NO. CA971623

Reactions of Carboxylic Acids on Oxides

1. Selective Hydrogenation of Acetic Acid to Acetaldehyde

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Received August 18, 1995; revised January 2, 1997; accepted January 24, 1997

Acetic acid has been used as a model compound in the selective hydrogenation of aliphatic acids, which contain α-hydrogen atoms, to their corresponding aldehydes. In contrast to what the literature predicts, it appeared to be possible to produce acetaldehyde directly from acetic acid. The appropriate catalyst consists of an oxide with an intermediate metal–oxygen bond strength. Addition of platinum to the catalyst enhances selectivity and activity. A mechanism is proposed, based on the involvement of lattice oxygen (viz., a Mars and Van Krevelen mechanism) and the spill-over of activated hydrogen from the platinum to the oxide. The most important side reaction is the formation of acetone from two molecules of acetic acid (ketonization), but this reaction is suppressed completely by the addition of platinum to the catalyst.

INTRODUCTION

Aldehydes are frequently used in the chemical and food industries, either as flavors and fragrances or as intermediates in various syntheses, such as the production of dyes, agrochemicals, and pharmaceuticals. Most aldehyde synthesis methods, however, produce large (stoichiometric) amounts of waste. It would, therefore, be desirable to develop a synthesis method that produces no or negligible amounts of waste and starts from cheap raw materials. As they are readily available from natural resources or easy to synthesize, carboxylic acids would be attractive raw materials for the production of aldehydes. Therefore, waste-free direct catalytic hydrogenation of carboxylic acids to aldehydes would be a very desirable reaction.

All the literature concerning selective hydrogenation of carboxylic acids describes the reaction of acids without α-hydrogen atoms, such as the hydrogenation of aromatic acids over the oxides of yttrium (1, 2), zirconium (with or without chromia added) (3–6), iron (7), vanadium (8), and manganese (9, 10) and the hydrogenation of trimethylacetic acid over the oxides of iron, manganese, or zirconium (7, 9, 11, 12). It is noteworthy that the same literature mentions that selective hydrogenation of acids with α-hydrogen atoms is virtually impossible.

The research reported in this paper is an attempt to investigate the possibility of a direct reduction to aldehydes of aliphatic acids, including those containing α-hydrogen atoms. If such a synthesis method is indeed possible, it is also desirable to elucidate the mechanisms involved and to establish the conditions necessary for high selectivity. Acetic acid is taken here as a model compound, since it is the simplest acid having α-hydrogen atoms. Moreover, a vast amount of knowledge has been collected about the behavior of acetic acid on single-crystal oxide surfaces (13–22) and on oxide powders at reduced pressure (23–29).

METHODS

The acetic acid used was obtained from J. T. Baker, Holland (99–100%). The oxides used were γ-Al_2O_3 (Degussa, Germany); Bi_2O_3, CuO, MgO, PbO_2, ZrO_2 (Merck, Germany); Co_3O_4, Cr_2O_3, V_2O_5, ZnO (BDH, England); α-Fe_2O_3, SnO_2, WO_3 (Fluka, Switzerland); GeO_2 (ex $GeCl_4$, Janssen, The Netherlands); MnO_2 (Aldrich, USA); NiO [ex $Ni(NO_3)_2 \cdot 6H_2O$, Baker, USA]; and TiO_2 (Tioxide, England). They were used as powders without any *ex situ* pretreatment. *In situ*, the oxides were heated for 1 h in a hydrogen flow at 100°C. Oxide-supported platinum catalysts were prepared by wet impregnation. The precursor [$H_2Pt(OH)_6$, Johnson Matthey, England] was dissolved in dilute nitric acid prior to the impregnation. The standard atomic ratio between the platinum and the cations in the oxide was 0.05. Before use, the platinum-containing catalysts were pretreated *ex situ* in an oxygen flow (5 h, 400°C) and subsequently in a hydrogen flow (4 h, 400°C).

A series of Pt/TiO_2 catalysts with different metal loadings were prepared by gently mixing, without applying any pressure, a standard Pt/TiO_2 catalyst (Pt/Ti ratio = 1/10) with the appropriate amount of pure titania. This standard catalyst was obtained by wet impregnation of the platinum from a boiling nonacidified water solution of the precursor. Both the Pt/TiO_2 and pure titania were subjected to the same

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treatment, i.e., calcination (oxygen flow, 5 h, 450°C) and reduction (hydrogen flow, 4 h, 300°C), before mixing.

An ^{18}O-labeled tin oxide was prepared by partial reduction of tin oxide (450°C, 30 min, in a hydrogen flow) and subsequent reoxidation at 200°C with labeled oxygen (Isotec Matheson, USA, 98%).

All catalytic experiments were performed in a flow system at slightly elevated pressure (total pressure: 1.2 bar). A hydrogen flow (90 ml/min) was saturated with acetic acid at room temperature (saturation pressure of 25 mbar) and led over a microreactor containing 0.2 g of catalyst. During the reaction, the temperature was raised from room temperature to 450°C at the rate of 7°C/min and subsequently lowered to 200°C at the rate of 10°C/min. Analysis was made quasi-continuously with a mass spectrometer (Balzers QMG 064). The recorded values were corrected for overlapping fragmentation peaks and for the mass spectrometer sensitivity by the method described by Ko *et al.* (30). The following products were monitored simultaneously: methane, carbon monoxide, carbon dioxide, water, ketene, acetone (2-propanone), acetaldehyde (ethanal), ethanol, ethene, ethane, and propene. When the term *aldehyde* is used in the following text, it can be read as acetaldehyde.

Selectivity (S), yield (Y), and conversion (α) were calculated in terms of numbers of carbon atoms, according to the following equations, where p_i is the partial pressure and c_i is the number of carbon atoms of product i:

$$S_i(\%) = \frac{p_i c_i}{\sum_{\text{products}} p_i c_i} \cdot 100\%,$$

$$Y_i(\%) = \frac{p_i c_i}{p_{\text{acid, initial}} c_{\text{acid}}} \cdot 100\%,$$

$$\alpha = \frac{\sum_{\text{products}} p_i c_i}{p_{\text{acid, initial}} c_{\text{acid}}}.$$

RESULTS

Oxide Catalysts

In the following figures, the partial pressures of acetic acid and its most important products are plotted as a function of temperature. Arrowheads are added to the curves to distinguish between the results of the increasing temperature program and the subsequent decreasing temperature regime. Figure 1 refers to titania catalyst, from which it can be concluded that titania is a good catalyst for the ketonization reaction:

$$2\mathrm{CH_3COOH} \rightarrow \mathrm{CH_3COCH_3} + \mathrm{CO_2} + \mathrm{H_2O}. \quad [1]$$

The ratios found coincide approximately with the reaction of two molecules of acetic acid to form one molecule each of acetone, carbon dioxide, and water. The reaction runs above 300°C, and no other products are detected. The oxides γ-alumina, chromia, and zirconia exhibit a catalytic behavior very similar to that of titania.

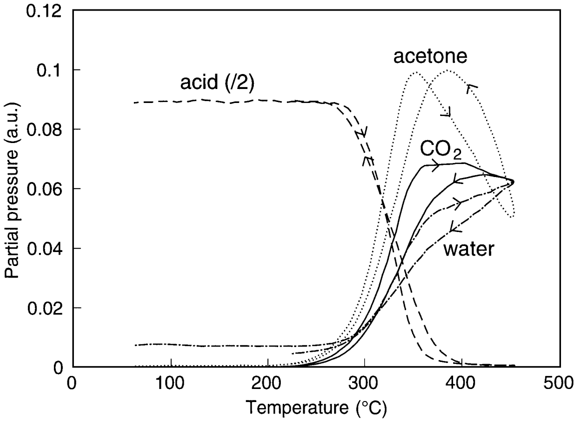


FIG. 1. Partial pressures of acetic acid and products in the reaction over pure TiO_2 under standard conditions. (The acetic acid signal is divided by 2 to fit the figure.)

Figure 2 shows the result of the reaction over copper oxide. The black-green copper(II) catalyst precursor was reduced by the reaction mixture to red copper(I) oxide or metallic copper, above about 225°C. The small increase in the water signal between 225 and 320°C was a consequence of this (Fig. 2). Immediately after this (partial) reduction of the catalyst, acetaldehyde and water were formed. Small quantities of ethanol and methane were also formed, but these are not shown in the figure. Almost no acetone and CO_2 were produced. During the decreasing temperature program, the catalyst was slightly less active. X-ray diffraction (XRD) analysis of the used catalyst showed only the presence of copper metal; however, metallic copper, obtained from *in situ* prereduced copper oxide, showed no catalytic activity in a standard temperature-programmed experiment.

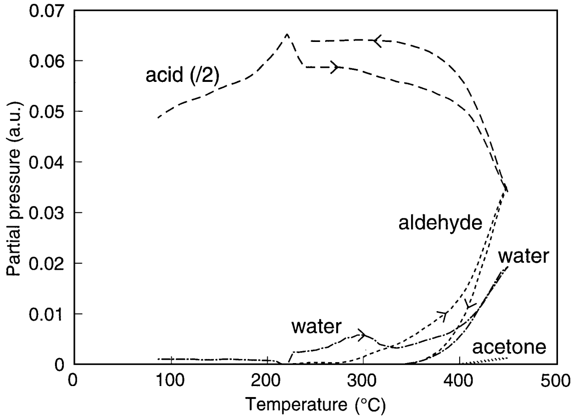


FIG. 2. Partial pressures of acetic acid and products in the reaction over pure CuO under standard conditions. (The acetic acid signal is divided by 2.)

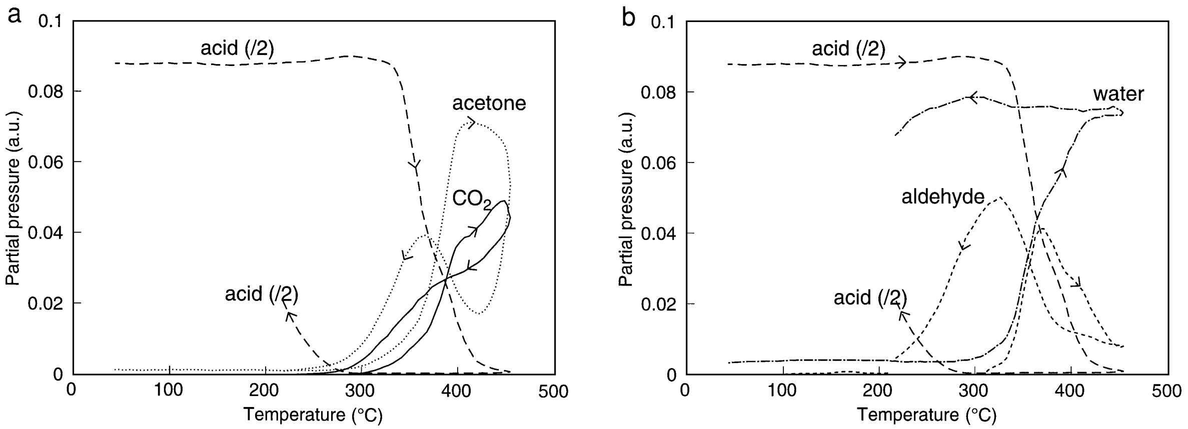


FIG. 3. Partial pressures of acetic acid and products in the reaction over pure α-Fe_2O_3 under standard conditions. (The acetic acid signal is divided by 2.)

Figure 3 shows the product pattern obtained with iron oxide. During the increasing temperature program, the reaction over iron oxide produced mainly acetone with CO_2 and water and small quantities of aldehyde; however, with decreasing temperature, i.e., after 450°C had been reached, acetaldehyde was the main product. Furthermore, the catalyst was active at lower temperatures. *Ex situ* XRD analysis showed that, after the standard temperature program was completed, the catalyst consisted of a mixture of Fe_3O_4 and α-Fe.

To compare the different oxides, the maximum aldehyde selectivities are given in Fig. 4. They are displayed as a function of metal–oxygen bond strength, which is calculated per oxygen atom from the heat of formation $-\Delta H_0$ of the highest oxide. Oxygen bond strength is used here only in a qualitative manner as a way to display and order the results. It should be mentioned that in all cases except copper, the main by-product is acetone. Some oxides were completely reduced to zero-valent metals during the temperature-programmed reaction. The metals formed in this way appeared to be either inactive, e.g., bismuth, lead, and copper, or very unselective, e.g., nickel, which is a good methanation catalyst.

Reaction Site

Titania catalyst was prereduced in hydrogen at different temperatures. Two things occurred when the prereduction temperature was increased. First, the surface area of the catalyst decreased, causing a decline in total activity. Second, aldehyde was formed when the catalyst was prereduced at temperatures exceeding 600°C. Below this temperature acetone was the only product formed. In Fig. 5 the ratio of the two main products, acetone and aldehyde, is given as a function of the prereduction temperature.

According to XRD analysis, the titania used as starting material consisted of anatase. The heating required for

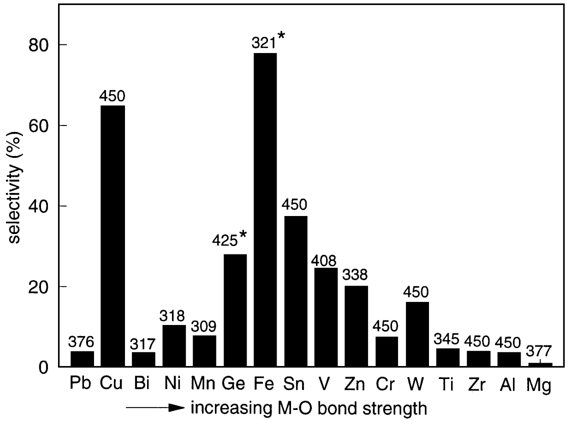


FIG. 4. Plot of maximum selectivity as a function of increasing (not on scale) metal–oxygen bond strength. Above each bar is given the temperature (°C) at which this selectivity is reached. When the selectivity was obtained at decreasing temperature, this is marked with a star.

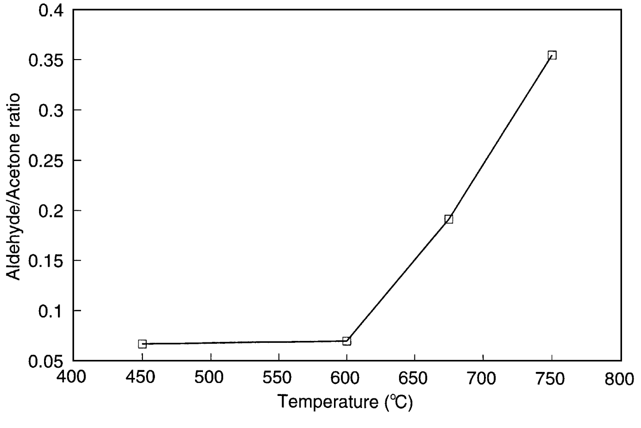


FIG. 5. Molecular ratio of aldehyde to acetone in the reaction of acetic acid over titania as a function of prereduction temperature (reduction in a hydrogen flow for 2 h). The reaction temperature was 375°C, the ratio being determined after 1000 s of reaction on stream.

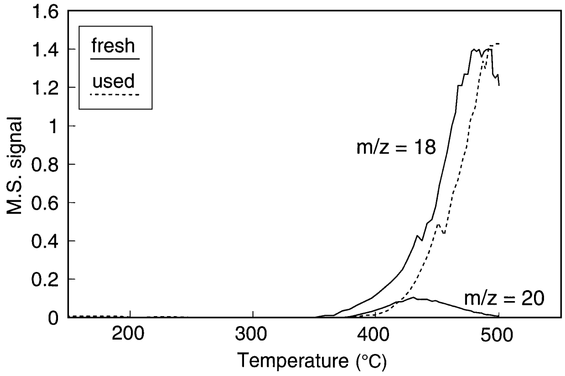


FIG. 6. TPR of a partly oxygen-labeled tin oxide catalyst in a reaction with acetic acid in hydrogen at 350°C. The mass spectrometer signals of water (H_2O, $m/z = 18$) and labeled water ($H_2{}^{18}O$, $m/z = 20$) are shown as a function of the reduction temperature.

prereduction caused a transformation into a rutile structure. This transformation was complete at a temperature above which the ratio of acetaldehyde to acetone could still be increased by further reduction.

Figure 6 shows the results of an experiment performed to test the possible participation of lattice oxygen in the reaction. Here, a partly ^{18}O-labeled tin oxide, which had been used in a reaction of acetic acid with hydrogen for 17 h at 350°C, was subjected to thermally programmed reduction (TPR). The reaction temperature used was the lowest at which a reaction of acetic acid to acetaldehyde was found to occur. For comparison, a fresh catalyst was also subjected to TPR. Before both TPR experiments, the catalyst was outgassed for 1 h at 350°C in helium.

TPR of the fresh catalyst shows that the formation of both labeled ($m/z = 20$) and unlabeled ($m/z = 18$) water started below 400°C. The signal of the former had a maximum at 430°C; the signal of the latter just below 500°C. After reaction with the acetic acid/hydrogen mixture, all the labeled oxygen disappeared, and the reduction peak of unlabeled water appeared at a slightly elevated temperature.

Platinum/Oxide Catalysts

To investigate the influence of a metal on the catalytic behavior of oxides, platinum was added to various oxides. The precious metal platinum was chosen because it is known to remain in the metallic form under reaction conditions. This is not the case for less noble metals, which can easily be oxidized by oxygen-containing molecules present in the reaction mixture.

The activity of the pure platinum catalyst was tested first. This was done by depositing the metal on inert silica (Aerosil 300, Degussa, Germany). The results obtained with this catalyst are presented in Fig. 7. At 350°C the acetic acid signal decreased and the reaction products detected were mainly methane, water, CO, and CO_2, obtained from the total decomposition of acetic acid. Acetaldehyde was also detected in very small quantities.

When platinum was added to oxides other than the inert silica, a drastic change in the behavior, compared with both Pt/SiO_2 and the pure oxides was seen. As an example, the results of a catalytic test over Pt/titania are shown in Fig. 8. When a comparison is made between Pt/TiO_2 and Pt/SiO_2, there are two remarkable differences. First, the temperature at which the reaction started was lower with the former catalyst. Second, hydrogenation products, such as acetaldehyde, ethanol, and ethane, were formed on Pt/TiO_2. The differences with the pure titania, however, are even more striking. While ketonization was the only reaction seen on pure titania (Fig. 1), on Pt/TiO_2 no acetone was formed at all. At 450°C, water reached its saturation pressure at ambient temperature and subsequently condensed in the flow system. A constant water signal, corresponding to the saturation pressure, was recorded at decreasing temperatures. As acetic acid dissolved in this condensed water, no acetic acid signal was observed at decreasing temperatures.

In Fig. 9 the maximum selectivities of several Pt/oxide systems are plotted as a function of increasing metal–oxygen bond strength. For comparison, the results obtained with

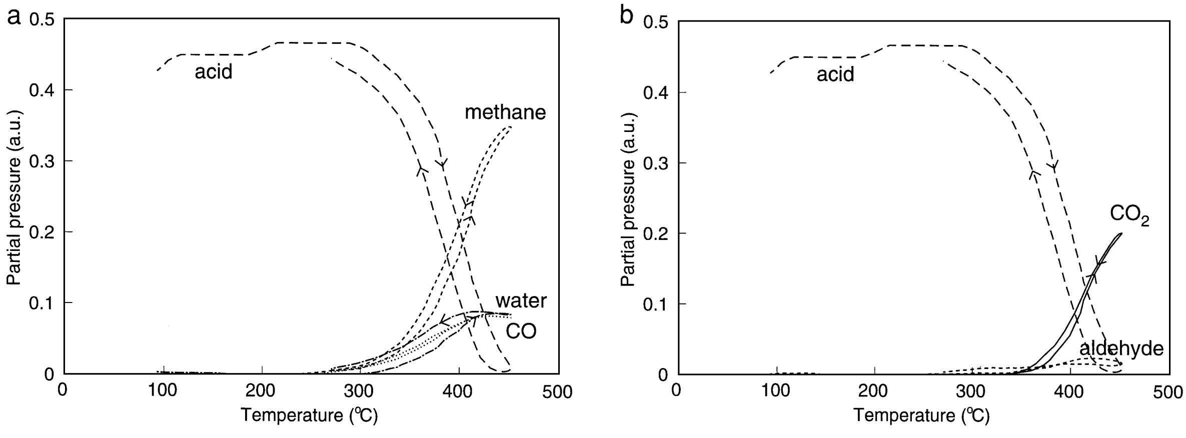


FIG. 7. Partial pressures of acetic acid and products in the reaction over Pt/silica under standard conditions.

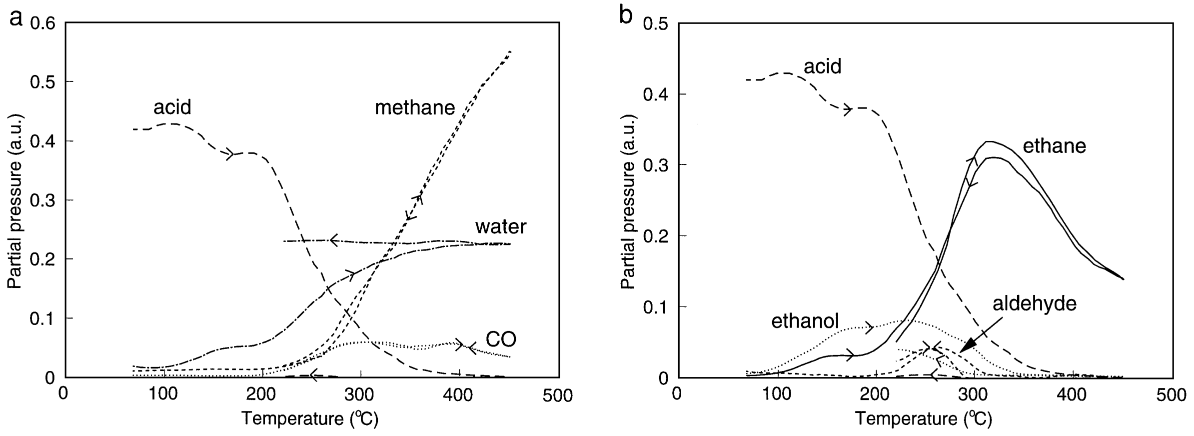


FIG. 8. Partial pressures of acetic acid and products in the reaction over Pt/titania under standard conditions.

the pure oxides are also presented in the same graph. On the pure oxides, acetone was the main by-product. Nevertheless, no acetone at all was formed when platinum was added to the oxides. Manganese oxide was the only exception; its catalytic selectivity was hardly affected by the addition of platinum.

When a system containing both a metal and an oxide is used as a catalyst, it is interesting to determine the specific function of each component of the catalyst. To elucidate this a series of titania catalysts with varying platinum loadings were tested for activity and selectivity. This catalytic system was chosen as titania cannot be reduced to its metallic state under the conditions used, not even in the presence of platinum. This ensures the presence of a metallic as well as an oxidic component during the reaction. In Fig. 10, the amount of catalyst used was varied in such a way that the amount of platinum in the reactor remained constant. All the results shown in this figure are therefore, obtained with a constant metal content but with a varying amount of titanium oxide. As can be seen, the overall activity clearly increased with increasing oxide content.

In Fig. 11, the results presented are those obtained with a constant amount of oxide and, thus, with a varying metal content. No correlation was found between metal content and conversion. All catalysts were found to have comparable catalytic activity.

In Fig. 12 the specific acetaldehyde yield at 425°C is presented for the same series of measurements as described above. Increasing the amount of oxide has a positive effect on aldehyde production. An increase in platinum loading has a negative effect. The decrease in aldehyde yield is accompanied by an increase in the volume of the decomposition products CO_2, CO, and CH_4. The catalyst with the lowest platinum loading deviated from this trend. This catalyst also produced some acetone, the formation of which is characteristic of pure titania. In this context, one other

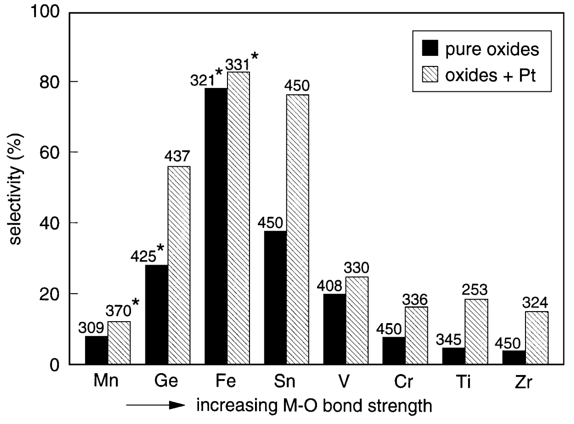


FIG. 9. Plot of maximum selectivity as a function of increasing metal–oxygen bond strength. Above each bar is given the temperature (°C) at which this selectivity is reached. When the selectivity was obtained at decreasing temperature, this is marked with a star.

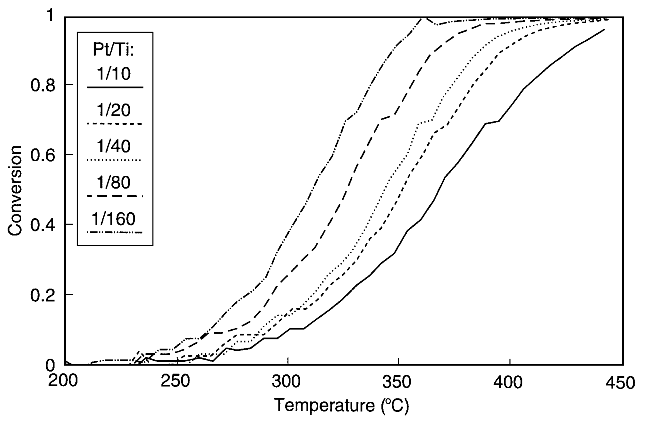


FIG. 10. Total conversion of Pt/TiO_2 catalysts with varying metal loadings (given as molar ratios). Series with constant platinum and varying TiO_2 content. (The amount of TiO_2 increases when going from the "1/10" to the "1/160" catalyst.)

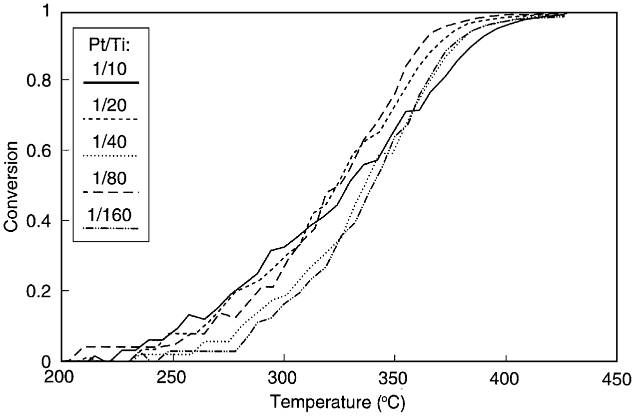


FIG. 11. Total conversion of Pt/TiO_2 catalysts with varying metal loading (given as molar ratios). Series with constant TiO_2 and varying platinum content. (The amount of Pt decreases when going from the "1/10" to the "1/160" catalyst.)

result is worth mentioning. To test the importance of direct contact between the platinum and titania, a Pt/silica catalyst (such as was used for the experiment presented in Fig. 7) was mixed gently with titania. The catalytic behavior of this mixed catalyst was very similar to that of the just-described Pt/titania catalysts prepared by wet impregnation. All products formed on the Pt/titania catalyst, except ethane, were also formed on this catalyst consisting of Pt/silica mixed with titania. On both catalyst systems, no acetone was produced.

DISCUSSION

Oxidic Catalysts and Reaction Site

With a properly selected catalyst, hydrogenation of acetic acid to acetaldehyde appeared to be possible, even though this acid contains three α-hydrogen atoms. This is at variance with the claims in the patent literature (5–10) that carboxylic acids having two or more α-hydrogen atoms are ketonized instead of hydrogenated.

It is indeed true that most oxides catalyze the ketonization reaction to acetone, carbon dioxide, and water; however, some oxides, especially those of copper, iron, tin, and vanadium, give a reasonable yield of acetaldehyde. The property these oxides have in common is the ability to change their oxidation state rather easily. The importance of this feature is stressed by the observation that these oxides are active in the hydrogenation of acetic acid to acetaldehyde in a temperature range where partial reduction of the catalyst has taken place. This is most obvious for copper(II) oxide, which, just before the reaction of acetic acid started, was transformed into copper(I) oxide. This transformation was indicated by the change in color accompanied by a peak in the water signal around 300°C (Fig. 2). Also, the oxides of tin, vanadium, and iron are active at temperatures at which in a hydrogen atmosphere less oxidized forms such as SnO, VO_2, and Fe_3O_4 are stable. This was even more clearly proven for iron oxide by *ex situ* XRD analysis and *in situ* Mössbauer spectroscopy experiments (31).

The idea that redox properties could be important is supported by Figs. 4 and 9 where the selectivity is displayed and ordered according to the metal–oxygen bond strength of the catalysts. Here it can be seen that oxides with either very high or very low metal–oxygen bond strength (except copper) are not selective. This can be explained by the theory proposed by Mars and Van Krevelen (32). In this theory lattice oxygen plays an active role in two steps of the catalytic reaction. In the first step, lattice oxygen reacts with a reducing adsorbate, i.e., hydrogen. The reaction product, water, desorbs and an oxygen vacancy is created (reaction [2a]). In the second step, this vacancy is refilled by an oxygen from the oxidant, i.e., acetic acid. The

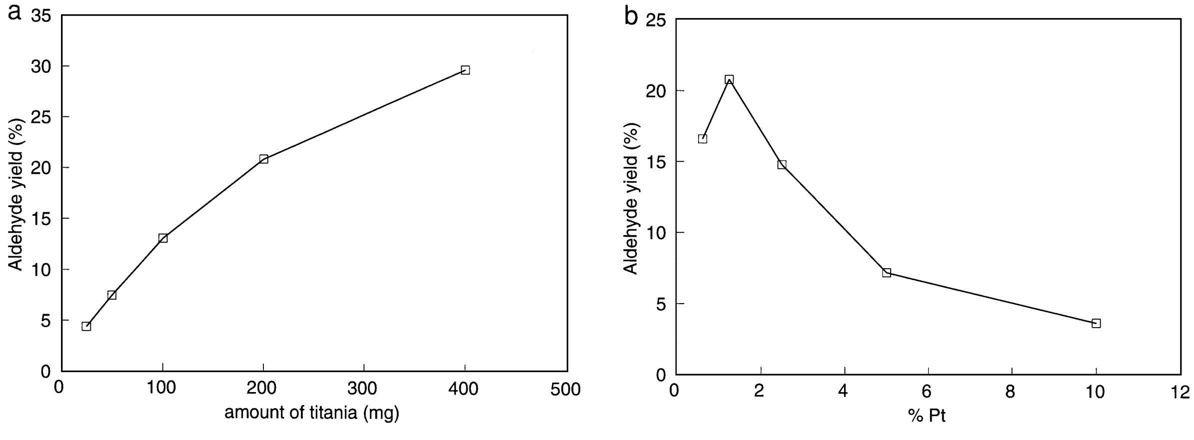
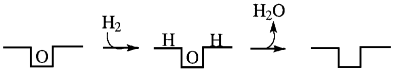
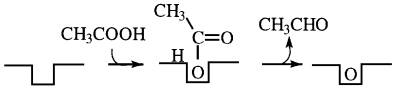


FIG. 12. (a) Aldehyde yield (*Y*) obtained with Pt/TiO_2 catalysts with varying amounts of titania at 425°C. (Series with constant platinum and a varying TiO_2 content.) (b) Aldehyde yield (*Y*) obtained with Pt/TiO_2 catalysts with varying metal loading (given as at.% Pt) at 425°C. (Series with constant TiO_2 and varying platinum content.)

surface species that results can easily react to acetaldehyde (reaction [2b]).



[2a]



[2b]

If metal–oxygen bond strength is too high, the first step will be very slow, as the oxygen is too strongly bound to the lattice and vacancies are not easily created. If metal–oxygen bond strength is too low, the second step will limit the reaction, since the affinity of the lattice for oxygen is too low to extract oxygen from an oxygen-containing molecule. Thus, the best catalyst for a reaction that runs by this mechanism is an oxide with intermediate metal–oxygen bond strength.

By oxygen labeling experiments an attempt has been made to find support for the involvement of the Mars–Van Krevelen mechanism.

TPR of the fresh ^{18}O-enriched tin oxide catalyst (Fig. 6) showed reduction peaks for both unlabeled and labeled water. Two facts can be deduced from the positions of the maxima and the relative heights of these peaks. First, only a small percentage of the lattice oxygen had been exchanged with labeled oxygen, and, second, the labeled oxygen was localized on easily reducible sites, which are probably located at the surface. After reaction with acetic acid, the reduction peak of the labeled water completely disappeared and the peak of unlabeled water shifted to higher temperatures. This means that during the reaction, the easily removable oxygen atoms, most probably surface atoms, are extracted from the lattice. This agrees with a Mars–Van Krevelen mechanism. Some caution, however, is necessary. It appeared that the reaction of acetic acid to aldehyde always starts at the same temperature as the reduction of the oxide. On one hand, this indicates that the Mars–Van Krevelen mechanism can operate, since the first step in this mechanism is a partial reduction of the catalyst creating oxygen vacancies. On the other hand, it complicates oxygen labeling experiments, since the removal of labeled oxygen from the lattice can be caused by the hydrogenation reaction (via Mars and Van Krevelen) or by a simple reduction of the oxide running in parallel. In any case, the fact that hydrogenation of the acid is always accompanied by reduction of the catalyst surface, suggests the need for oxygen vacancies in this reaction.

This suggestion is further confirmed by the results obtained with the reaction of acetic acid over prereduced titania (Fig. 5). This catalyst had been taken as a model, since it is well documented that oxygen vacancies are created by reduction (33). An increase in reduction temperature can, therefore, be correlated directly to an increase in the number of oxygen vacancies, which apparently favors aldehyde formation. This strongly indicates that oxygen vacancies are needed for the deoxygenation step of the selective hydrogenation of acetic acid to acetaldehyde.

Platinum/Oxide Catalysts

Copper clearly deviates in its behavior from the other catalysts (Fig. 4). During the temperature-programmed reaction, the very selective formation of acetaldehyde started shortly after copper had been reduced, i.e., at 300°C (Fig. 2). In a hydrogen atmosphere, both CuO and Cu_2O are unstable at these temperatures; however, pure metallic copper appeared to be completely inactive. Hence, the catalyst must be, at least partly, in an oxidic state if its reactivity above 300°C is to be explained. Obviously, the reaction mixture is less strongly reducing than pure hydrogen. This enables the catalyst surface to remain partly oxidized and, therefore, stay active and selective.

XRD analysis of the used iron oxide catalyst, which was also highly selective, revealed the simultaneous existence of Fe^{3+}, Fe^{2+}, and Fe^0. Thus, although pure metals seem to be unselective or even completely inactive, a mixture of an oxide with a metal, as found for iron and copper, seems to be very selective. This also explains why iron and copper exhibit high selectivity, which deviates from the volcano-like correlation in Fig. 4.

To investigate further the effect of combining a metal with an oxide, oxide-supported platinum catalysts were tested. Platinum supported on inert silica was taken as a model for pure platinum. This system appeared to be very active, but only in the total decomposition of acetic acid (Fig. 7). The molar ratios of the products found suggest the existence of two decomposition routes with the following overall equations:

$$CH_3COOH \rightarrow CH_4 + CO_2, \qquad [3]$$

$$CH_3COOH + H_2 \rightarrow CH_4 + CO + H_2O. \qquad [4]$$

The addition of platinum to an oxide drastically changes the behavior of both the platinum and the oxide. The combination produces aldehyde to a larger extent and at lower temperatures than it does the individual components. The complete absence of acetone formation when more than 2 at.% platinum is added is remarkable, too. Instead of the ketonization, hydrogenation and decomposition products are formed. The only exception is the Pt/manganese oxide system. Pure manganese produces acetone via a bulk-salt decomposition reaction instead of a catalytic surface reaction (34). Apparently, this reaction route to acetone is not affected by the addition of platinum, whereas the surface reaction to acetone, which occurs on the other oxides tested here, is completely suppressed.

At first glance, five reasonable explanations can be put forward to describe the above-mentioned changes in catalytic behavior.

1. The presence of platinum causes complete reduction of the oxide. The resulting bimetallic system could have special catalytic properties.
2. A bifunctional mechanism is involved. First, acetone is formed on the oxide, just as it is on the pure oxide. Subsequently, all the acetone formed could react on the platinum to yield hydrogenation and decomposition products.
3. The reaction proceeds on the platinum surface, whose properties are drastically changed by promotion effects of the oxide. It is possible that the oxide is deposited on the platinum surface during the preparation or migrates to the surface during pretreatment (the so-called strong metal–support interaction, SMSI).
4. The reaction proceeds on the oxide surface, whose properties are changed by the presence of activated hydrogen supplied by the platinum via so-called spill-over.
5. The reaction proceeds at the interface between the metal and the oxide. At this interface special catalytic properties could arise, e.g., by the stabilization of ionic platinum.

The idea of a bimetallic catalyst can be rejected. Oxides such as zirconia and titania cannot be reduced to metal at the temperatures used, not even in the presence of platinum (35). Zinc oxide or tin oxide can be reduced and can very readily form alloys with platinum (36, 37); however, results obtained earlier (38) indicate than an oxidized phase is necessary to achieve high selectivity to aldehyde.

Although acetone, when led over a Pt/titania catalyst, can form some aldehyde, the second possibility is unlikely for two reasons. First, CO_2 production always attends the formation of acetone; however, CO_2 is almost never observed among the products of the reaction over Pt/oxide catalysts. The consecutive reaction of acetone, therefore, cannot explain the product distribution found. Second, this mechanism should also be applicable to acetone formed by bulk acetate decomposition; however, the acetone formed on manganese oxide does not react with the platinum added.

The third and fifth possibilities, the oxide-promoted metal or the metal–oxide interface as the reaction site, are in principle both acceptable. Nevertheless, many arguments support the fourth possibility, viz., the oxide as the locus of reaction. Let us now discuss them.

First, by the addition of platinum, the formation of acetone is completely suppressed at temperatures at which the pure oxides are active in the ketonization reaction (compare, e.g., titania, Fig. 1, with Pt/titania, Fig. 8). This indicates that either the behavior of the oxide is completely changed or no acetic acid ever has a chance to react on the oxide because it is consumed immediately by a reaction on the metal or on the metal–oxide interface. Since acetone formation is also suppressed at conversions lower than 100%, when not all the acid is consumed, the latter explanation is incorrect. The reaction is most likely to proceed on the oxide surface, whose properties are completely changed by the presence of neighboring platinum.

Second, the plot of selectivity as a function of metal–oxygen bond strength has a volcano-shaped form, with or without platinum added (see Figs. 4 and 9). This indicates that, in both cases, the reaction proceeds via the same kind of mechanism, viz., a Mars–Van Krevelen mechanism, and thus occurs on the oxidic surface.

Third, the Pt/silica catalyst mixed with titania behaved comparably to Pt/titania, although in the mixed catalyst there is most probably less close contact between the titania and the platinum. Therefore, the reaction cannot proceed on the platinum/titania close-contact interface or on the titania-promoted metal, as neither of these sites is present in the mixed catalyst.

The last, but certainly not the least, argument supporting the idea that the desired deoxygenation reaction proceeds on the oxide can be deduced from Figs. 10 and 11. It can be seen there that total conversion is directly related to the amount of oxide, but is independent of the amount of platinum. As the interface area is directly proportional to the amount of platinum, it can be concluded that total conversion is also independent of interface area.

Figure 12 shows the specific aldehyde yield. An increasing amount of oxide has a positive influence on aldehyde yield (Fig. 12a). Figure 12b shows that the use of increasing amounts of platinum has even a negative effect on aldehyde yield. In the latter case, optimum yield is attained with a 1.25 at.% platinum catalyst (Pt/Ti ratio = 1/80). Higher loadings induce the formation of larger amounts of decomposition products, probably because acetic acid or its hydrogenation products decompose on the platinum (see Fig. 7). A lower loading does not eliminate acetone formation completely, because there is not enough platinum to spread its influence over the entire catalyst surface.

Concluding, not only the overall reaction, but also the selective hydrogenation to acetaldehyde, proceeds most probably on the oxidic surface. Addition of platinum suppresses acetone formation. A very high platinum content enhances side or consecutive reactions to decomposition products. A very low platinum content does not eliminate acetone formation completely. With catalysts prepared as described above, the optimum is found at a loading of 1.25 at.% platinum.

Reaction Mechanism

The just-mentioned findings can be interpreted as follows. Oxides are not very active in hydrogen activation. Deposited platinum can activate hydrogen, which subsequently migrates to the oxide surface by a spill-over mechanism. In this way reactions that occur on the oxide surface

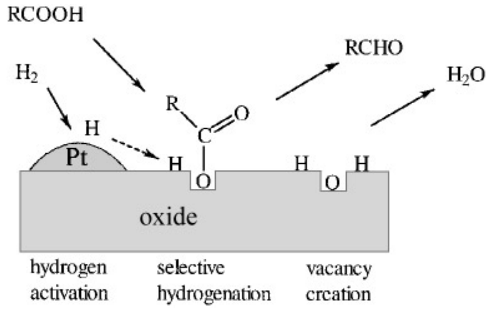


FIG. 13. Schematic representation of the proposed reaction steps in the selective hydrogenation of acetic acid to acetaldehyde.

and need hydrogen can proceed at lower temperatures and are favored over reactions that do not consume hydrogen, such as ketonization. Hence, activity and selectivity of oxides for deoxygenation reactions can be enhanced by the addition of platinum.

Evidence of spill-over effects in catalysis has accumulated in recent years (39–46). Nevertheless, there is still some dispute about the exact influence spill-over has. Although spilt-over hydrogen diffuses fast and can be found at a distance of 1 cm from its origin (41), Delmon argues that the supply of spilt-over hydrogen can never account for stoichiometric consumption in a catalytic reaction (42). He suggests that hydrogen spill-over mainly alters the steady-state structure of the oxide surface and, thus, influences catalytic activity only indirectly. Other authors, however, suggest that spilt-over species are not only responsible for creating specific catalytic sites but are also reactants themselves (44, 45). Whatever the origin of the effect is, the idea of hydrogen spill-over neatly explains the data collected here and can therefore be advanced as a basis for a satisfactory explanation. Nevertheless, it should be mentioned that prereduction of TiO_2, i.e., the creation of extra sites before the actual reaction takes place, has a durable, i.e., a catalytic and not a stoichiometric, effect on selectivity (Fig. 5). This indicates that a mere site creation by spilt-over hydrogen could be enough to explain an increase in selectivity during the steady state of the reaction.

Summarizing the mechanisms proposed, a schematic representation can be composed for the selective hydrogenation of acetic acid to acetaldehyde (Fig. 13). Platinum activates the hydrogen, which migrates to the oxide, where the actual reaction takes place. The spilt-over hydrogen can be used either as a reactant in the hydrogenation reaction or to keep the steady-state concentration of oxygen vacancies at a constant level.

CONCLUSIONS

In contradiction to what the literature claims, acetic acid can be reduced to acetaldehyde, even though this acid contains three α-hydrogen atoms. Copper oxide and oxides with intermediate metal–oxygen bond strength, such as iron oxide and tin oxide, are the best catalysts for this selective hydrogenation (i.e., deoxygenation).

The volcano-shaped dependence of selectivity on metal–oxygen bond strength and the fact that the best catalysts can easily change their oxidation state suggest a possible role for the Mars–Van Krevelen mechanism. Oxygen labeling experiments seem to support this mechanism. Furthermore, the presence of oxygen vacancies is proven to be beneficial for a high selectivity to aldehyde. The involvement of a Mars–Van Krevelen type of mechanism is, therefore, very likely.

Metals are not active in the selective hydrogenation; however, a combination of metal and oxide was found to favor acetaldehyde formation strongly. Platinum combined with an oxide exhibits higher activity and selectivity than does the platinum or the oxide separately. The formation of acetone is suppressed by the presence of platinum. The reaction site seems to be the oxide and not the metal. The metal probably serves for the activation of hydrogen, which subsequently migrates to the oxide. This spilt-over hydrogen enhances the activity and selectivity for all reactions on the oxide that need hydrogen, including acetaldehyde formation.

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