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Selective Reduction of Acetic Acid to Acetaldehyde on Iron Oxides

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The selective reduction of acetic acid to acetaldehyde on iron oxides has been studied in various pressure ranges. A good selectivity towards acetaldehyde could be achieved with molecular hydrogen continuously present in the gas phase and on a prereduced catalyst containing both a metal phase (zero-valent metal) and an oxidic phase. The pressure of acetic acid appears to influence the formation and the kind of by-products. At low pressures of acetic acid (0.015 mbar) ketene ($CH_2{=}C{=}O$) is the most important (by-)product, while at high pressures (25 mbar) ketene has never been observed and acetone is the main (by-) product. Reaction mechanisms have been proposed for the selective reduction to acetaldehyde and for the formation of the (by-)products. Presumably the reduction to acetaldehyde occurs on the vacancy-rich oxidic layer, while hydrogen is dissociated on the zero-valent metal sites. The by-products are most likely formed via a common ketene-like intermediate. © 1994 Academic Press, Inc.

INTRODUCTION

Hydrogenation or reduction of carboxylic acids to the corresponding aldehydes is of great industrial importance. Aldehydes are important organic building blocks for the production of perfumes, pharmaceutical- and agrochemical products. The industrial interest is for instance demonstrated by the desire to develop new waste free technologies for the production of insecticides (using aromatic carboxylic acids as raw materials) (1, 2). Until now one of the most used ways to produce aldehydes is the Rosenmund reduction of carboxylic acids (3). Since this reaction produces a considerable amount of waste, a replacement of the Rosenmund reduction by a direct gas phase reduction by hydrogen is desirable. This has only been successful for carboxylic acids without any α-hydrogen atoms (i.e., no hydrogen on the carbon atom next to the carboxylic group, e.g., benzoic acid) (4–8).

Apart from the industrial interest, carboxylic acids are also a subject of research from a fundamental point of view. For a long time, formic acid is used to test the dehydrogenating and dehydrating power of catalysts (e.g., 9–11). With acetic acid a large number of decomposition experiments at low pressures have been described in literature (12–18). It has been found that acetic acid can be adsorbed dissociatively to form a surface acetate, which can desorb again as acetic acid or decompose. Vajo *et al.* (19) reported the formation of ketene from acetic acid on polycristalline platinum covered with carbon. In all these papers, describing experiments in high vacuum systems, no appreciable quantities of aldehydes have been reported. Just a few studies deal with reactions other than decomposition at atmospheric conditions. Since long, ketonisation of acids is known to occur over different oxidic catalysts (e.g. 20–22). The reaction of acetic acid on sodium exchanged zeolite (23) resulted in the production of ketene, while Sabatier and Mailhe and Davies and Hodgson (24, 25) described the production of aldehydes from acids using formic acid as a reducing agent and titanium oxide as a catalyst. Kuriacose and Jewur (26) are the only authors who have studied the reaction of acetic acid with hydrogen on an iron oxide catalyst. Acetone and ketene were the products mentioned in their paper and no formation of acetaldehyde has been reported.

So far either decomposition reactions or formation of ketene and acetone has been found both at low pressure reactions as well as during reactions at higher (ambient) pressure. Very few of these experiments have been performed in a hydrogen atmosphere. Only few authors (23) were able to produce aldehydes using an external hydrogen source. Therefore, it seems interesting to study the behaviour of catalysts in reactions of acetic acid with and without hydrogen both at low as well as at atmospheric pressure, with particular attention to the formation of acetaldehyde from acetic acid. Exploratory experiments in our laboratory with a series of oxides revealed that iron oxide is a very promising catalyst. This paper reports the results obtained so far.

METHODS

The starting material for all iron oxide catalysts prepared is Fe_2O_3 (Fluka Chemika, Switzerland). Fe_3O_4 has been prepared by reduction of Fe_2O_3 in flowing hydrogen (4 h, 1013 mbar) at different temperatures. XRD analysis

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showed that reduction of Fe_2O_3 at 400°C resulted in a sample containing only Fe_3O_4 (code: $Fe_3O_4(400)$). The catalyst contained a mixture of Fe_3O_4 and Fe^0 when the reduction temperature was increased to 450°C (code: $Fe_3O_4(450)$). At reduction temperatures higher than 450°C Fe^0 prevails. XRD analysis proved the existence of Fe^0 only at the higher reduction temperatures ($T_{red} > 400°C$). A slightly oxidized sample (code: $Fe_3O_{4+x}(400)$; $0 < x \leq 0.5$) has been prepared by in situ oxidation of $Fe_3O_4(400)$ (1 hour, 1 mbar O_2(99,998% Messer Griesheim, Germany), 400°C). The information about the composition of the different phases is in full agreement with that in Ref. (26). As long as the reaction temperature did not exceed the pretreatment temperature no difference was seen between the XRD data before and after the experiments.

Measurements at Atmospheric Pressure

Steady state catalytic experiments have been performed in a continuous flow system, working at slightly elevated pressure (1.2 bar). A hydrogen flow (90 ml/min) was saturated with acetic acid (99–100% purity, J.T. Baker B.V., Holland) at room temperature (saturation pressure of about 25 mbar) and passed through a microreactor containing 0.2 g of catalyst. During the reaction the temperature was raised from room temperature to 450°C at a rate of 7°C/min and subsequently lowered to 200°C at a rate of 10°C/min. Analysis of the gas phase has been done quasi continuously by a quadrupole mass spectrometer (Balzers QMG 064). The recorded values have been corrected for overlapping fragmentation peaks and product sensitivity. The appearance of the following products has been recorded: methane, carbon monoxide, carbon dioxide, water, ketene, acetone, acetaldehyde, ethanol, ethene, and propene. The selectivity is calculated from the balance in carbon atoms.

Measurements at Low Pressure

Batch experiments at low pressure have been performed in an all-glass static vacuum system (lowest pressure $1 \cdot 10^{-8}$ mbar) connected to a magnetic sector mass spectrometer (VG Instruments MM8-80s) via a stainless steel tube and a fine control leak valve (VG Instruments MD6). The vacuum system was suited for admission of gases and vapours of liquids and solids. The pressure of acetic acid in the gas phase was approximately 0.015 mbar in each experiment. When hydrogen was present in the gas phase the following sequence of admitting the gases has been used:

(1) admission of 0.015 mbar acetic acid at room temperature; (2) equilibration of gas phase and adsorbed layer (1 min); (3) admission of H_2 (99,9990% purity, Messer Griesheim, Germany) up to $\approx$ 0.600 mbar total pressure. The excess of hydrogen is approximately 40-fold. The experiments have been performed as temperature programmed reactions, the temperature being raised from 25 to 400°C at a rate of 5°C/min. Since no reaction took place in all experiments below 180°C, all figures show the results in the temperature range 180–400°C. The collected mass spectrometric data have been corrected for overlapping fragmentation peaks. The corrected partial pressures used in the figures are in arbitrary units and have not been converted into real units of pressure (mbar).

Units used: $y°C = (273 + y)$ K; 1 mbar = 100 Pa.

RESULTS

Measurements at Low Pressure

Figures 1 to 4 show the results of temperature programmed reactions of acetic acid on $Fe_3O_4(400)$ or its oxidized form $Fe_3O_{4+x}(400)$. Figure 1 shows the results obtained with the oxidized form, $Fe_3O_{4+x}(400)$. In the experiment shown here, no hydrogen has been admitted to the gas phase.

CH_3CHO (acetaldehyde) and HCHO (formaldehyde) are the most important products, having a desorption maximum at approximately 300°C. Also the amount of methane is high. Ketene desorbs at about 260°C in relatively small amount, while hardly any acetone is produced. The partial pressure of CO_2 exceeds the maximum measurable concentration already at 300°C, indicating a high capability for oxidation by this catalyst. Oxidizing this catalyst in O_2 after several consecutive TPR experiments did not result in the production of either CO or CO_2, indicating that on Fe_3O_{4+x} *no* deposition of a carbonaceous layer took place.

In situ reduction of the oxidized catalyst has been performed either by prolonged evacuation at 400°C or by a short reduction with H_2 (30 min, 400°C). A temperature programmed reaction of acetic acid without hydrogen

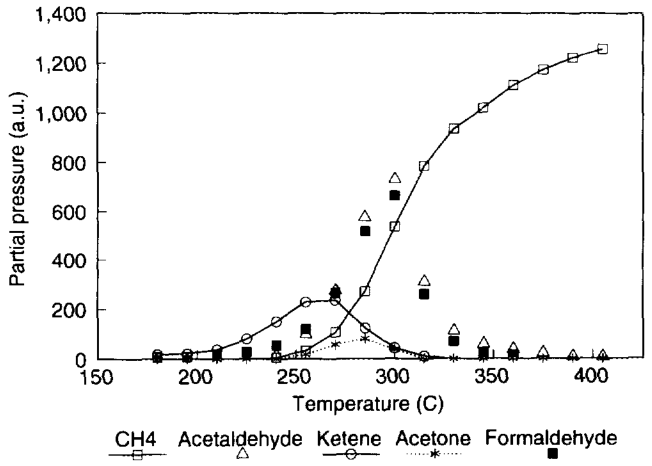


FIG. 1. Temperature programmed reaction of acetic acid on $Fe_3O_{4+x}(400)$.

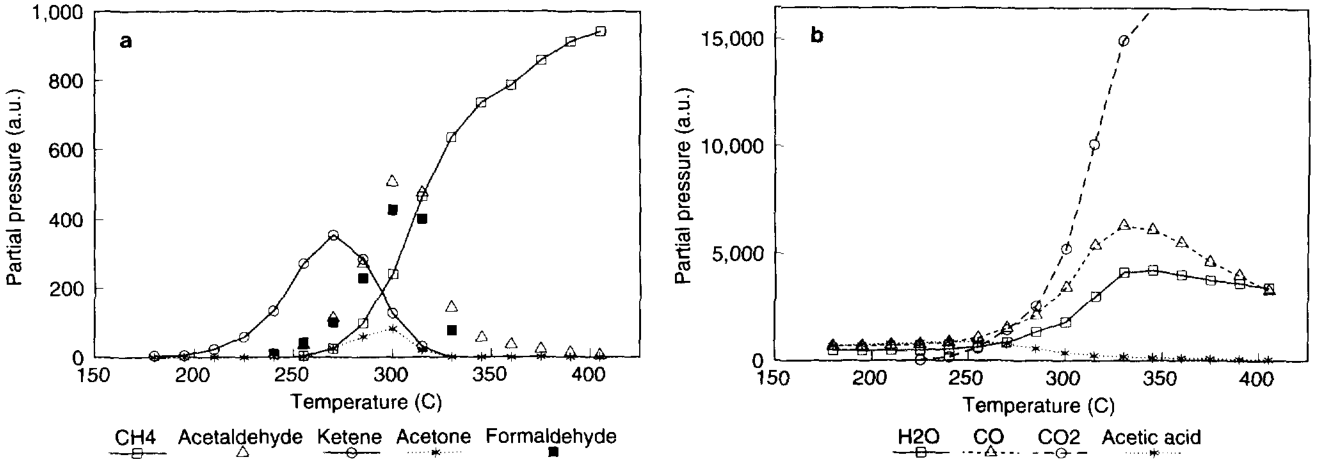


FIG. 2. Temperature programmed reaction of acetic acid on Fe_3O_4(400); (a) formation of CH_4, HCHO, CH_3CHO, $CH_2{=}C{=}O$ and $(CH_3)_2C{=}O$; (b) formation of H_2O, CO, CO_2.

present in the gas phase resulted in an increasing production of ketene compared to acetaldehyde and formaldehyde (Fig. 2a). The desorption maxima occur at approximately the same temperatures as in the previous experiment. From 350°C onwards, the CO_2 concentration comes out of the measuring range of the mass spectrometer (Fig. 2b).

Figures 3 and 4 show the results of consecutive TPR experiments of acetic acid and hydrogen on Fe_3O_4 (400). The catalyst has only been evacuated after the experiment described in figure 2 (evacuated at 400°C for 15 min followed by evacuation at 25°C for 15 h). The same evacuation sequence is used between the experiments described in Figs. 3 and 4.

It can be seen in Fig. 3 that with hydrogen present in the gas phase the production of acetaldehyde and formaldehyde is suppressed, while the amount of ketene remains high. The amount of CO_2 decreases (not shown) and the concentration of CH_4 is lowered simultaneously with the concentration of acetaldehyde. Furthermore, it looks as if the desorption maxima shift to higher temperatures: ketene to 330°C and acetone and aldehydes to 375°C.

The presence of hydrogen does not lead to the formation of acetaldehyde from acetic acid or one of the surface intermediates. This is seen again in Fig. 4 where the results of a consecutive experiment of acetic acid and hydrogen have been presented. The concentration of acetone rises compared to that of ketene and even exceeds it. The partial pressures of acetaldehyde and CH_4 are almost zero. The desorption maxima for ketene and acetone occur at about 330 and 375°C, respectively.

Figure 5 shows the results of a temperature programmed reaction of acetic acid on Fe_3O_4(450). The differ-

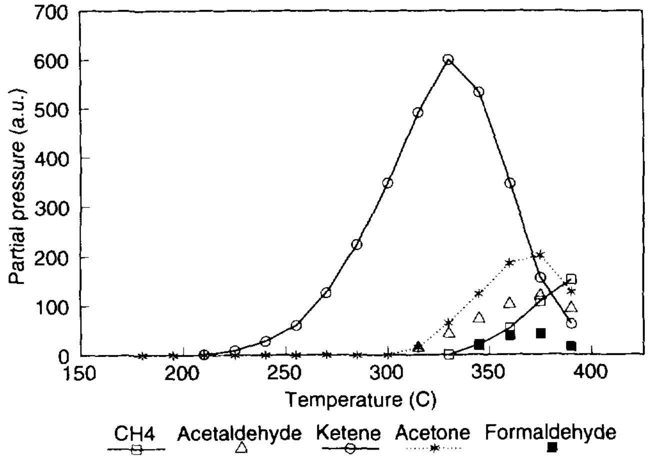


FIG. 3. Temperature programmed reaction of acetic acid and hydrogen on Fe_3O_4(400).

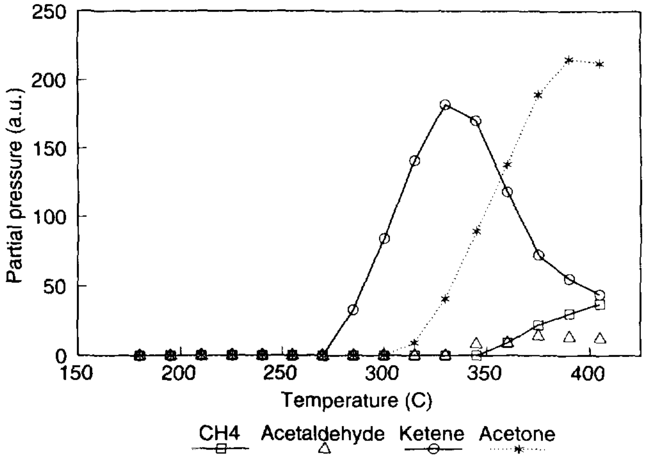


FIG. 4. Temperature programmed reaction of acetic acid and hydrogen on Fe_3O_4(400) (results of a consecutive experiment performed immediately after the experiment described in Fig. 3).

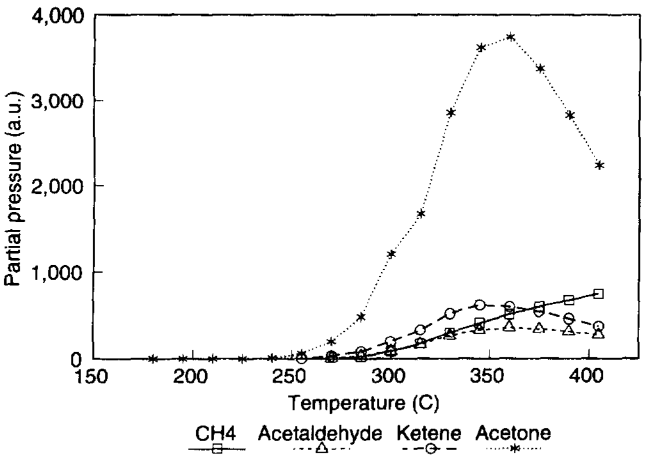


FIG. 5. TPR of acetic acid on Fe_3O_4(450).

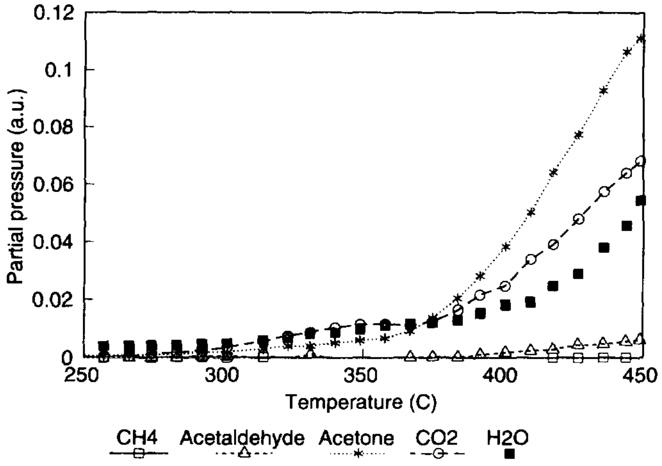


FIG. 7. Fe_3O_4(400), product pattern in helium.

ences with all of the previous experiments are striking, mainly when H_2 is present in the gas phase. Acetone is the main product formed, having a desorption maximum around 360°C. The concentration of CO_2 (not shown) is also high and rises simultaneously with that of acetone. Methane, ketene, and acetaldehyde have low gas phase concentrations. At temperatures higher than 365°C the peak named "ketene" consists now not only of ketene but also of propene.

In Fig. 6 the results of the temperature programmed reaction of acetic acid *with hydrogen* on Fe_3O_4 (450) have been depicted. Acetaldehyde is the first product to desorb followed by the desorption of acetone (325 and 375°C). The concentration of ketene remains low, however the amount of methane has risen considerably compared to Fig. 5. The formation of CO_2 is suppressed, CO now being the most important oxidation/decomposition product (not shown).

Measurements at Atmospheric Pressure

Figures 7 and 8 show the results of temperature programmed reactions of acetic acid in helium and hydrogen on Fe_3O_4(400).

In both cases acetone is formed together with CO_2 and H_2O. Up to 400°C Figs. 7 and 8 show a very similar behaviour. At temperatures above 400°C and with hydrogen in the gas phase (Fig. 8), the reaction of acetic acid occurs together with the reduction of the oxide. This results in a decrease of the acetone and CO_2 production and an increase in the production of acetaldehyde and methane.

Figures 9 and 10 show the results of temperature programmed reactions of acetic acid in helium and hydrogen on Fe_3O_4(450).

Fe_3O_4(450) shows a higher activity than Fe_3O_4(400), both with and without hydrogen in the stream. When

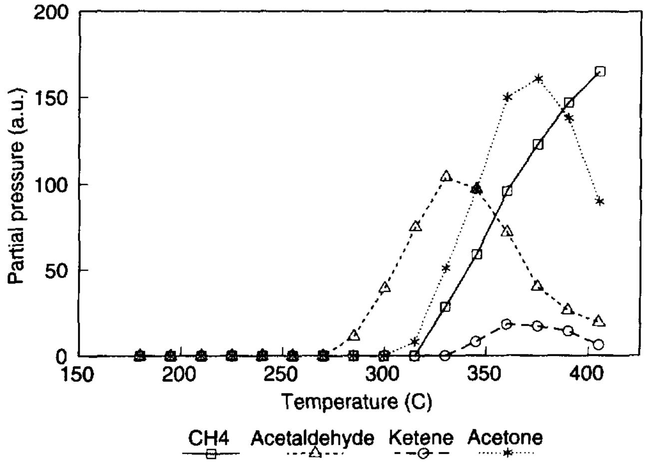


FIG. 6. TPR of acetic acid and hydrogen on Fe_3O_4(450).

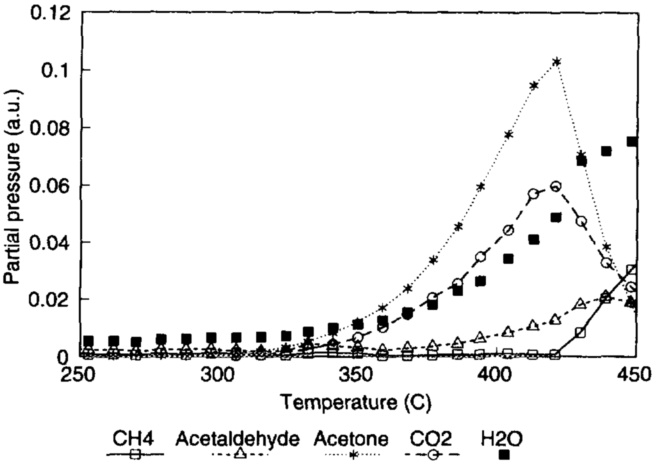


FIG. 8. Fe_3O_4(400), product pattern in hydrogen.

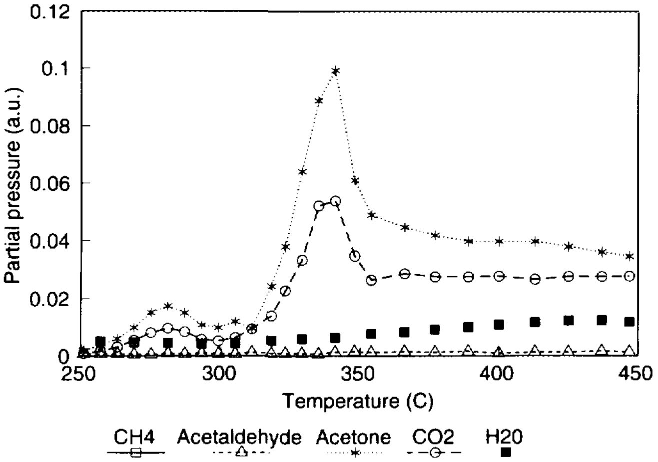


FIG. 9. $Fe_3O_4(450)$, product pattern in helium.

helium is used as a carrier gas acetone is the main product (Fig. 9). Figure 10 shows that when hydrogen is present a good selectivity towards acetaldehyde can be achieved; above 360°C the methane production increases strongly.

The importance of hydrogen is further demonstrated in Fig. 11. The carrier gas has been switched from hydrogen to helium during a reaction at constant temperature over iron oxide ($Fe_3O_4(450)$). In a hydrogen flow mainly acetaldehyde is produced, while in helium acetone is the main product.

The above-presented results show a clear dependence of the selectivity towards acetaldehyde on the reduction temperature of the catalyst. Figure 12 shows the influence of the reduction temperature (before the catalytic experiment) on the selectivity in the experiments at atmospheric pressure.

Unreduced iron oxide shows a poor selectivity for acetaldehyde, but when the reduction temperature exceeds 400°C a large amount of acetaldehyde is produced. At even higher temperatures the selectivity decreases again.

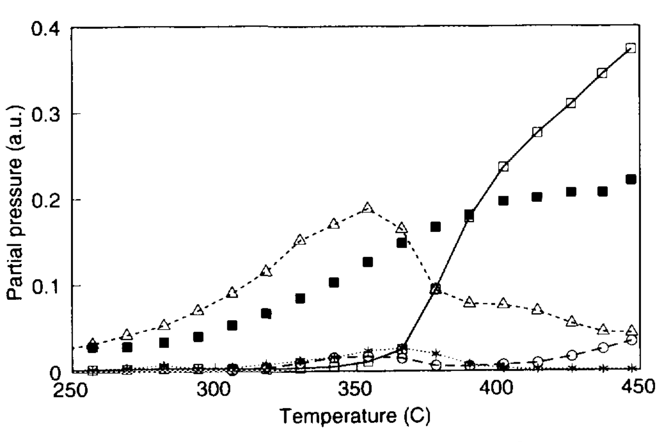


FIG. 10. $Fe_3O_4(450)$, product pattern in hydrogen.

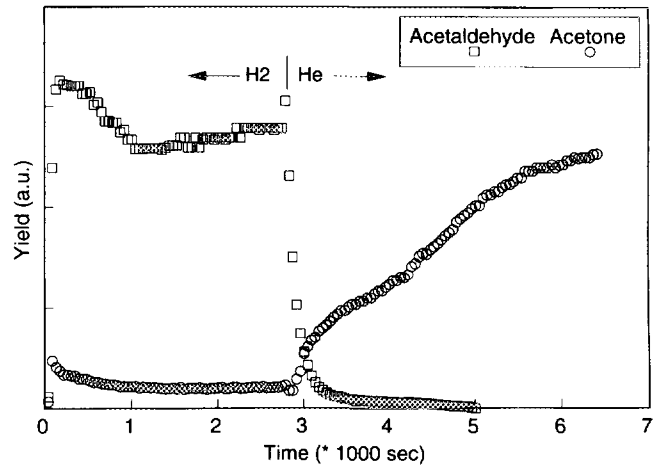


FIG. 11. Yields of acetone and acetaldehyde versus time. The carrier gas is changed from hydrogen to helium during the experiment. The catalyst is prereduced at 450°C.

DISCUSSION

In contrast to the statements in the already mentioned patents, it has been found that the catalytic production of aldehyde from a carboxylic acid, which contains α-hydrogen, is possible. However, pretreatment as well as reaction conditions have to be chosen very carefully in order to obtain a good yield of acetaldehyde from acetic acid.

By taking a look at Fig. 12 it can be concluded that the prereduced and the oxidized form of the catalyst lead to different products in steady state catalytic experiments. Acetone is by far the main product of the reaction of acetic acid over unreduced Fe_3O_4, but the more reduced forms of iron oxide produce preferentially acetaldehyde. These two products are most probably formed on different sites. The formation of the desired acetaldehyde requires the presence of a reduced oxidic surface site or zero-valent iron. In Fig. 11 information pointing in the same direction can be seen. The presence of certain sites before the reaction is a necessary, but not a sufficient condition for the selective reaction. The sites must also be kept active by hydrogen in the reaction mixture. Combining the results shown in Figs. 11 and 12, it can be concluded that the formation of acetaldehyde is only possible when sites with low valency iron are continuously regenerated by hydrogen.

The question arises whether the active site for aldehyde formation is a zero-valent metal atom alone or an oxidic layer, which covers the iron surface and contains many defects. It should be noted that under reaction conditions used two phenomena occur simultaneously. On one hand hydrogen keeps the formation of Fe^0 and Fe^{2+} going on, on the other hand acetic acid produces oxides by its decomposition on the iron surface (12). Furthermore, it is

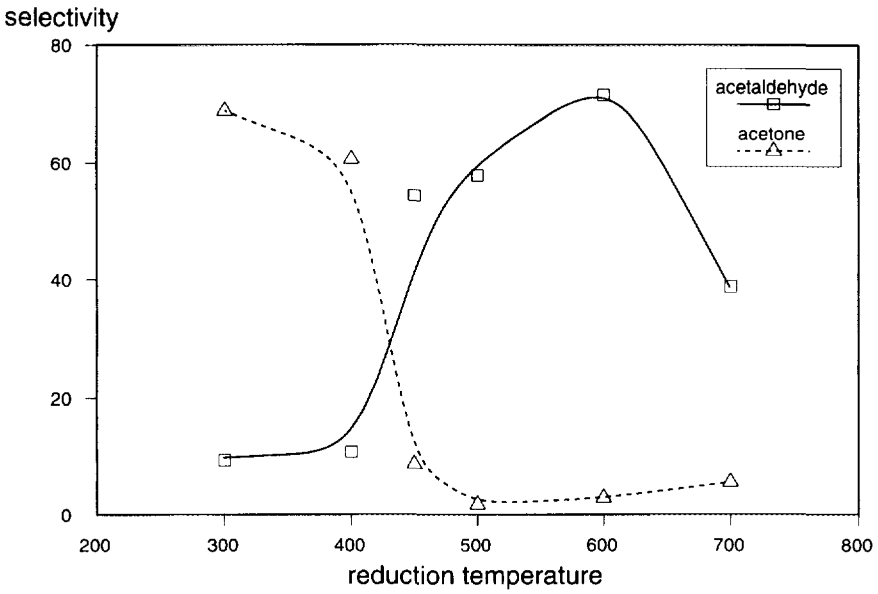


FIG. 12. Selectivity towards acetaldehyde and acetone versus the reduction temperature of Fe_2O_3. The reactions have been performed at 350°C.

known (26) that iron acetate decomposes into Fe_2O_3. The existence of an oxidic surface layer in the steady state can be accomplished by the mechanism just described.

At this moment it is difficult to answer definitively the question whether the zero-valent metal alone or an oxidic layer is the active site for the desired reaction to acetaldehyde. However, in the case of other oxides such as tin, nickel, or copper it is sure that a complete reduction of an oxide to the metal kills the desired reaction (27). Also platinum, a metal on which the formation of an oxidic layer from acetic acid and the subsequent stability of this layer in a hydrogen atmosphere are improbable, is completely unselective. But if platinum is covered by an oxide which is difficult to reduce, e.g. tin or germanium oxide, a selective catalyst is obtained, while Pt/Sn^0 alloy behaves more like pure Pt (27). In this context it is interesting that the Pt/FeO_x system, like other Pt/oxide systems, is selective and therefore Fe can probably exist in some sort of an oxidic layer even in close contact with Pt. When iron behaves like an oxide in the presence of platinum, it most likely behaves similarly in a pure iron catalyst. Therefore, the tentative conclusion may be drawn that, although the active catalyst contains mainly zero-valent iron as is seen by XRD, the oxidic layer is ((or participates in) the active site for the selective reduction of acetic acid. Possibly, the mechanism runs via a Mars and Van Krevelen-like mechanism (28). It is sure that the presence of a zero-valent metal improves the supply of atomic hydrogen (29, 30), which, as can be seen in Fig. 11, is required for the production of acetaldehyde. The following model is suggested to explain the selective reduction over iron oxide (Fig. 13):

By assuming this mechanism all results of the experiments under ambient pressure can be easily understood. The reaction of acetic acid in helium on Fe_3O_4(400) as well as on Fe_3O_4(450) produces acetone, CO_2 and H_2O, because no hydrogen, needed for the reduction of both the acid as well as the catalyst is present (Figs. 7 and 9). Fe_3O_4(400) in hydrogen behaves similar to Fe_3O_4(400) in helium as no hydrogen can be activated (Fig. 8) when zero-valent metal is not present on the surface. However, when the catalyst is reduced at higher temperature (Fe_3O_4(450), Fig. 10) and hydrogen is present in the reaction mixture, all the conditions for the selective reduction towards acetaldehyde are fulfilled. At too high reaction temperatures (>350°C) methane becomes an important by-product. Note that when Fe_3O_4(400) is used in hydrogen above 425°C (Fig. 8), the reaction pattern starts to resemble the distributions found with Fe_3O_4(450) (Fig. 10).

The same behaviour as described above for the atmospheric pressure reactions is seen at low pressures. Fe_3O_4(400) produces predominantly acetone in the pres-

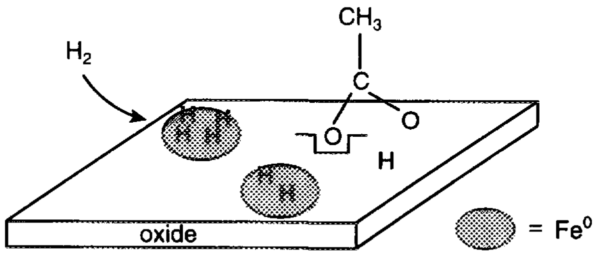


FIG. 13. Schematic representation of formation of acetaldehyde from acetic acid on Fe_3O_4(450), a catalyst containing Fe^0.

ence of hydrogen (Fig. 4). Also when Fe_3O_4(450) is used without hydrogen in the gas phase, acetone is the only product of importance. When Fe_3O_4(450) is used *with* hydrogen in the gas phase the concentration of acetaldehyde becomes considerably higher, acetone being still present but to a smaller extent. At higher temperatures methane becomes the most important product. Two differences can be seen when the experiments under low (i.e., batch) and high pressures (i.e., flow) are compared. First, in continuous flow experiments under ambient pressure no ketene has ever been detected, while under low pressures ketene formation is always observed. During the low pressure batch experiments, the partial pressure of ketene starts to drop as soon as the concentration of acetone starts to increase (Figs. 3 and 4). These results point to the idea that ketonization towards acetone is a consecutive reaction of ketene or its surface-bound precursor. This thought is supported by information from the literature. Ketene has been detected in low pressure experiments by several authors (19, 31, 32), while the authors who performed reactions of acetic acid at higher pressures only mention the formation of acetone (20–22, 26). Imanaka *et al.* (32) have shown that when an excess of acetic acid is admitted to a system containing adsorbed and gaseous ketene at a low pressure and a catalyst (CaO), the concentrations of both ketene and acetic acid decrease very rapidly (see Fig. 3 in Ref. (32)). The product of this reaction is acetone. This explains our different results at low and high pressure. With a high acetic acid pressure (25 mbar) ketene can not desorb but reacts immediately with acetic acid or acetate to acetone. When the acetic acid pressure is low ketene can desorb and be detected in the gas phase. The difference in acetic acid pressure (25 vs 0.015 mbar) is responsible for the presence or absence of ketene in the gas phase.

For the sake of completeness it should be mentioned that according to Barteau (33) the production of acetone is the result of a reaction between two coadsorbed acetic acid molecules/acetates. As suggested it is a plausible mechanism, but it is not helpful in explaining our results (and some literature results) in which ketene is a desorbing intermediate or in which the reaction of ketene with acetic acid is proven (32).

The second remarkable difference between the two kinds of experimental procedures is the formation of acetaldehyde on Fe_3O_4(400) at low pressure of acetic acid and without hydrogen (Figs. 1–3). A similar experiment under atmospheric pressure (using He as carrier gas) does not show any acetaldehyde production. It is striking that not only acetaldehyde but also formaldehyde is formed. Having the simultaneous production of ketene in mind, the formation of formaldehyde can be explained in the same way as done by Angevaare *et al.* (34). The authors (34) reported that adsorption of CH_3NO_2 on transition metal oxides leads to the formation of a nitronate anion $(CH_2{=}NO_2)^-$ already at room temperature. At elevated temperatures this nitronate anion is easily decomposed and reacts with surface oxygen to formaldehyde, N_2 and nitrogen oxides. Obviously, the C=N bond is very easily broken when attacked by oxygen. It can be expected that the same sort of reaction occurs in the case of ketene ($CH_2{=}C{=}O$), leading to formaldehyde. On the reduced surface less active oxygen is present to attack the C=C bond, resulting in a suppressed decomposition and increased desorption of ketene. This explains the difference between Fe_3O_{4+x}(400) and Fe_3O_4(400) as seen in Figs. 1 and 2: ketene desorbs from the reduced catalyst in higher amounts than from the oxidized catalyst. When hydrogen is added the decrease of formaldehyde formation and the increase of ketene production is even more pronounced (Fig. 3). The decrease in the oxidation capacity is also reflected by the decrease in the CO_2 production. The formation of acetaldehyde on Fe_3O_{4+x}(400) and Fe_3O_4(400) in experiments *without hydrogen* present in the gas phase can not be explained by the mechanism presented in Fig. 13. The amount of aldehyde is less than in the case of the reaction of acetic acid and hydrogen on Fe_3O_4(450), but it is well detectable. The formation of acetaldehyde on the two just mentioned catalysts can be explained with either of the two following pathways:

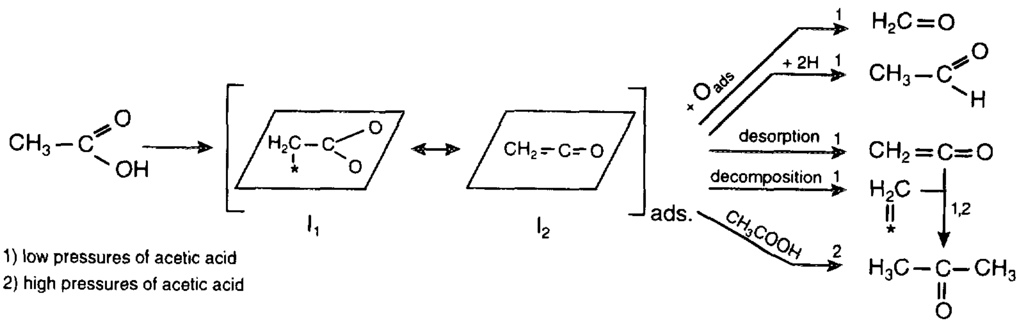
$$CH_3COOH \rightarrow CH_2{=}C{=}O\ (ad) + H_2O$$

$$CH_2{=}C{=}O\ (ad) + 2\ H\ (ad) \rightarrow CH_3CHO.$$

Ketene is no intermediate in the formation of acetaldehyde, but another reaction takes place

$$CH_3COO\ (ad) + 2\ H\ (ad) \rightarrow CH_3CHO + OH\ (ad).$$

With the already presented results in mind, it can be concluded that the first pathway is the most likely one. Ketene acts in this picture as an intermediate in the reaction of acetic acid to both formaldehyde (as described above) and acetaldehyde. Acetaldehyde and formaldehyde are produced at the same temperature and in comparable amounts (Figs. 1 and 2). When the reaction conditions are altered, e.g., as by going from Fig. 1 via 2 to 3, ketene production increases at the expense of the production of both acetaldehyde and formaldehyde. Ketene is decomposed less and its partial pressure rises compared to that of acetaldehyde and formaldehyde. However, acetaldehyde and formaldehyde keep to follow the same trend. Therefore, the mechanism with ketene as an intermediate seems to be the most likely pathway, although the other pathway still can not be excluded completely on the basis of the presently available results.



SCHEME 1

The following speculative Scheme 1 summarizes all presented results. To form ketene a hydrogen atom has to split off from the methyl group. This is only possible when the intermediate is adsorbed horizontally (e.g., I_1). This intermediate reacts to the products either directly or via intermediate I_2. To form acetone a C_1-unit has to be coupled to one of the intermediates. Such a C_1-unit (carbene species) can be formed by decomposition. Methane can be formed by the reaction of a methylene (CH_2) or methyl (CH_3) species with hydrogen.

CONCLUSIONS

It is possible to produce acetaldehyde from acetic acid over an iron oxide catalyst, although this is a carboxylic acid containing α-hydrogen atoms. The selectivity depends on the pretreatment of the catalyst and the reaction conditions. To produce acetaldehyde hydrogen must be present and the catalyst must be in a partly reduced form. This applies to experiments in the low and high pressure range. The simultaneous existence in the catalyst of Fe^0 sites (for dissociation of H_2) and oxygen vacancies in the oxidic part (existing continuously thanks to reduction by hydrogen) are responsible for the high selectivity and activity. Acetaldehyde is most likely selectively formed via a Mars and van Krevelen-like mechanism.

At ambient pressure acetone is the main product, when neither hydrogen nor a reduced form of iron oxide are present. At low pressure both ketene and acetone are seen in this case, the latter is probably produced by a consecutive reaction of the first mentioned molecule. In the low pressure experiments, acetaldehyde, formaldehyde and ketene are produced on an oxidized form of iron oxide (Fe_3O_{4+x}(400)) without hydrogen in the gas phase. All these products are probably formed via a common ketene-like intermediate.

ACKNOWLEDGMENT

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