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Influence of Oxygen and Iron in the Liquid-Phase Hydrogenation of α,β-Unsaturated Aldehydes

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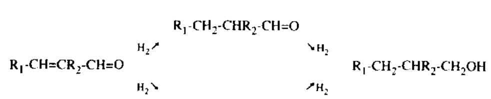
The effect of oxygen and $FeCl_2$ additions to the liquid-phase hydrogenation of the two α,β-unsaturated aldehydes, cinnamaldehyde and 2-ethyl-hexenal, was investigated over a Pt/Al_2O_3 catalyst. The addition of small amounts of oxygen to the feed considerably improved the activity in both the presence and absence of $FeCl_2$. Without oxygen and $FeCl_2$, the hydrogenation of 2-ethyl-hexenal to the saturated alcohol proceeded mainly via hydrogenation of the C=C double bond to yield the saturated aldehyde as intermediate. In the hydrogenation of cinnamaldehyde, on the other hand, the C=C and the C=O double bonds were hydrogenated at the same rate, yielding equal amounts of the saturated aldehyde and the unsaturated alcohol as intermediates. Addition of oxygen in the latter case increased the hydrogenation rate of the C=C double bond more than that of the C=O double bond, resulting in a decreased selectivity toward the unsaturated alcohol. The selectivity toward the unsaturated alcohol was in all cases enhanced by the addition of $FeCl_2$. High yields of the unsaturated alcohols were obtained by the addition of oxygen to the $FeCl_2$-promoted Pt/Al_2O_3 catalyst. The effect of $FeCl_2$ on the hydrogenations over a Pd/Al_2O_3 catalyst was also investigated. The unsaturated aldehydes were rapidly hydrogenated to the saturated aldehydes in both the presence and absence of $FeCl_2$. The further hydrogenation of the C=O double bond to the alcohols was extremely slow, but was somewhat increased by the addition of $FeCl_2$. No unsaturated alcohols were ever observed using the Pd/Al_2O_3 catalyst.

INTRODUCTION

There are two different possible first reaction steps in the consecutive hydrogenation of α,β-unsaturated aldehydes to saturated alcohols. Either the C=C double bond is hydrogenated to yield the saturated aldehyde as intermediate or the C=O double bond is hydrogenated to yield the unsaturated alcohol as intermediate (see below).



Industrially, the unsaturated aldehyde 2-ethyl-hexenal is hydrogenated to the saturated aldehyde and the saturated alcohol. The saturated aldehyde is then oxidized to octanoic acid, and the saturated alcohol is used for production of a plastic softener, dioctyl-phthalate. The unsaturated alcohol 2-ethyl-hexenol is not of commercial interest today.

Cinnamaldehyde and its corresponding unsaturated alcohol, saturated aldehyde, and saturated alcohol are all used in the perfume industry. Furthermore, the unsaturated alcohol is used as an intermediate in the production of some pharmaceuticals.

The catalyst of choice for complete hydrogenation to the saturated alcohols is either a nickel or a copper catalyst. With these catalysts, the reaction proceeds via hydrogenation of the C=C double bond to the saturated aldehydes and then further to the saturated alcohols. The saturated aldehydes can be obtained at high yields and at high

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rates using a palladium catalyst. The reaction stops almost completely after the hydrogenation of the C=C double bond. Whereas palladium is a perfect catalyst for hydrogenation to saturated aldehydes, there is no equally good catalyst known for selective hydrogenation of the C=O bond to unsaturated alcohols. However, relatively high yields of unsaturated alcohol can be obtained using platinum catalysts promoted with iron (*1–6*). Iron increases the reaction rate to unsaturated alcohol. The activity and the selectivity to unsaturated alcohol can also be improved by using promoters such as Sn^{4+}, Ge^{4+} (*4*), and Co^{3+} (*2*) or by supporting platinum on TiO_2 (*7*) or Nb_2O_5 (*8*).

A disadvantage in using platinum for hydrogenation of aldehydes is the very low activity. Platinum catalysts are excellent for hydrogenation of alkenes, but they deactivate very rapidly when used for hydrogenation of aldehydes. This is probably due to CO produced by decomposition of the aldehyde in a side reaction ($R\text{–}C{=}O \rightarrow R\text{–}H + CO$). The deactivation can, however, be prevented by the presence of small amounts of oxygen. This leads to production of CO_2 instead of CO (*9*).

In this work, the influence of both $FeCl_2$ and oxygen has been investigated in the liquid-phase hydrogenation of the α,β-unsaturated aldehydes 2-ethyl-hexenal and cinnamaldehyde on a Pt/Al_2O_3 catalyst. The effect of $FeCl_2$ has also been studied on a Pd/Al_2O_3 catalyst.

EXPERIMENTAL

Equipment

The experimental setup is shown in Fig. 1. The hydrogenations were performed in a baffled 0.75-liter stainless-steel slurry reactor which was heated by cartridge heaters in the reactor wall. The tightly sealed reactor had an internal stirrer. An external magnetic field provided the power to the stirrer shaft. The gas flows were regulated by mass-flow controllers and the pressure by a pressure controller at the gas outlet from the reactor. A condensor at the outlet prevented both loss of the solvent and damage to the pressure controller by the solvent. The overpressure in the reactor facilitated the sampling through a 1/8-in. tube.

Catalysts

Commercial catalysts were used in all experiments. These were a 0.5% Pt/Al_2O_3 (Aldrich 20,601-6) and a 0.5% Pd/Al_2O_3 (Aldrich 20,574-5) catalyst. The catalyst pellets were ground into a fine powder before adding to the reactor. The characteristics of the catalysts are given in Table 1.

Methods

One half liter of 99.5% ethanol and 10 g of the Pt/Al_2O_3 catalyst were added to the reactor. In the experiments with the Pd/Al_2O_3 catalyst, 5 g of the catalyst was used. The catalyst was then pretreated by passing hydrogen through the mixture at 4 bar and 323 K for 30 min. In the experiments with iron, $FeCl_2$ dissolved in ethanol was added and the mixture was treated with H_2 for another 30 min. Next, 5 ml of the reactant was added and the reaction started. The stirring speed was kept at 1000 rpm throughout all the experiments. The hydrogen pressure was 4 bar and the flow was kept at 550 ml/min. In the experiments with oxygen, air was mixed with the hydrogen to an O_2/H_2 ratio of 0.64%. The aliphatic aldehyde was hydrogenated at 323 K and the aromatic at 333 K. Samples were taken out during the hydrogenations and analyzed by a gas chromatograph (Varian 3300 supplied with a capillary column 30 m × 0.319 mm DB-5). The iron concentration in the solution was measured by atomic absorption spectrometry (Varian spectrAA-10).

While the data from these experiments are presented in the form of a table and graphs in two dimensions, it should be kept in mind that the results are three-dimensional since the selectivity and activity are functions of both independent variables, the iron and oxygen additions. Hence the presentation and the related discussion are con-

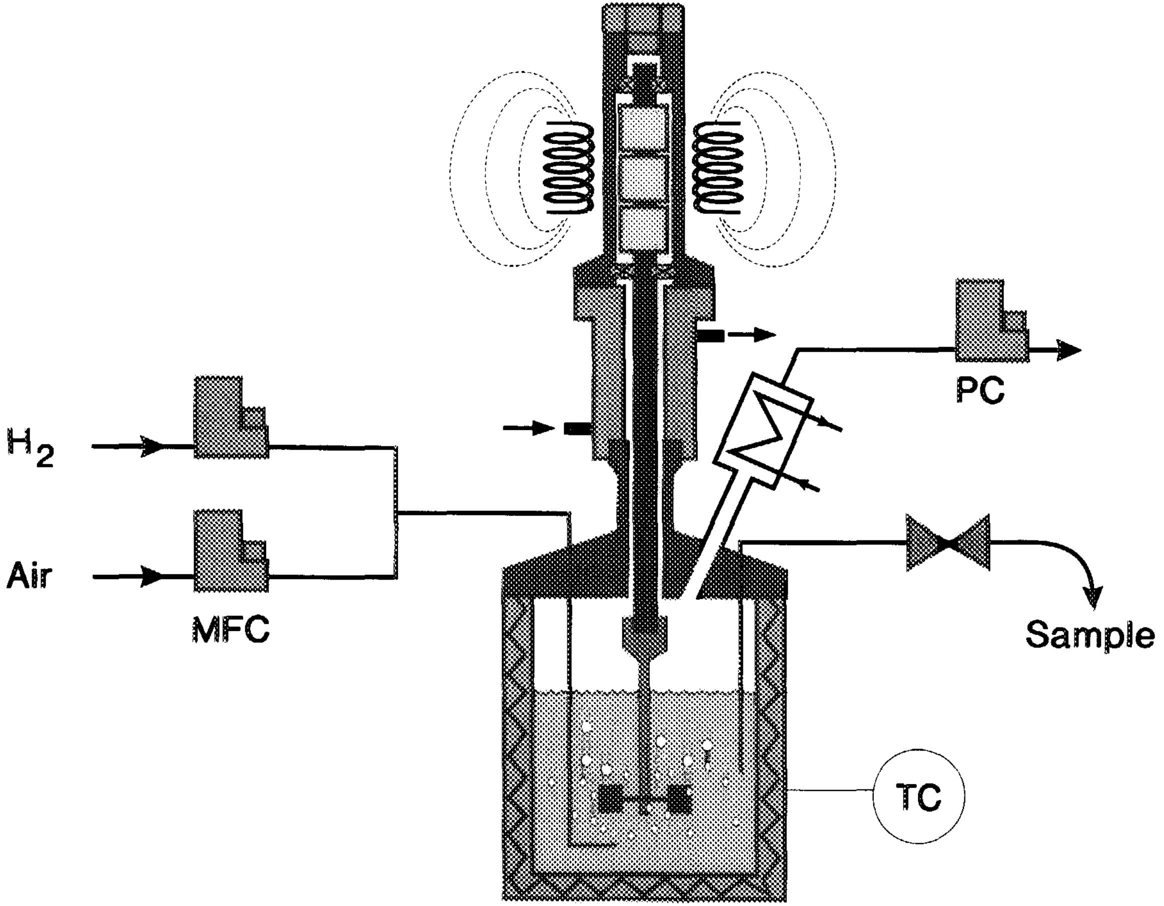

FIG. 1. Experimental setup.

TABLE 1

Catalyst Characterization

Catalyst	wt% metal	BET surface area (m^2/g)	Dispersion[a] (H/M)
Pt/Al_2O_3	0.55	109.6	0.47
Pd/Al_2O_3	0.5	82.1	0.64

[a] From hydrogen adsorption assuming a 1 : 1 H : M ratio.

cerned only with "cuts" through whole "surfaces" of data which can in principle be obtained by further measurements with the same procedures and accuracy as above.

RESULTS

Adsorption of Iron on the Pt Catalyst

Measurements of the iron concentration in the solution revealed that iron was adsorbed on the Pt catalyst. About 20% of the added amount of iron had been adsorbed on the Pt catalyst when the aldehyde was added after the pretreatment with hydrogen for 30 min (in the case where the added amount corresponded to Fe/Pt_s = 1; see definition below). The catalyst adsorbed iron even in the absence of H_2. However, the adsorption rate was somewhat increased by the presence of H_2.

Hydrogenation of 2-Ethyl-hexenal over Pt/Al_2O_3

The hydrogenation rate of 2-ethyl-hexenal over Pt/Al_2O_3 without addition of oxygen was extremely low in both the absence and presence of $FeCl_2$. Without $FeCl_2$, a high selectivity for the hydrogenation of the C=C double bond to the saturated aldehyde was obtained. The addition of $FeCl_2$ changed the selectivity toward hydrogenation of the C=O double bond yielding the unsaturated alcohol. The results are presented in Table 2. The selectivity is reported at 20% conversion and is defined as the moles of the actual product divided by the total moles of products obtained. Furthermore, the Fe/Pt_s ratio is defined as moles of added $FeCl_2$ per moles of exposed Pt atoms.

Addition of oxygen resulted in a much higher hydrogenation rate of 2-ethyl-hexenal over Pt/Al_2O_3 in both the presence and absence of $FeCl_2$. Without $FeCl_2$, mainly the C=C double bond was hydrogenated, giving a high yield of the saturated aldehyde. The addition of $FeCl_2$ increased the selectivity for hydrogenation of the C=O double bond, giving a high yield of the unsaturated alcohol. The activity was also increased at moderate $FeCl_2$ concentrations in the presence of oxygen. A maximum activity was obtained at an Fe/Pt_s ratio of 0.2. The results are presented in Figs. 2 and 3.

Hydrogenation of Cinnamaldehyde over Pt/Al_2O_3

The hydrogenation of cinnamaldehyde over Pt/Al_2O_3 without addition of oxygen was very slow and, compared to the hydrogenation of 2-ethyl-hexenal, the selectivity for the hydrogenation of the C=O double bond to the unsaturated alcohol was higher. In the absence of $FeCl_2$, the saturated aldehyde and the unsaturated alcohol were produced at the same rate. The selective hydrogenation of the C=O bond to the unsaturated alcohol was further enhanced by the addition of $FeCl_2$. The activity was also somewhat increased by the addition of $FeCl_2$.

Addition of oxygen resulted in a much higher activity, and the reaction path was changed toward hydrogenation of the C=C

TABLE 2

Hydrogenation of 2-Ethyl-hexenal without Oxygen over Pt/Al_2O_3

Fe/Pt_s[a]	TOF (s^{-1})	Selectivity (%)		
		Unsaturated alcohol	Saturated aldehyde	Saturated alcohol
0	0.007	13	65	22
0.27	0.003	51	12	37

[a] Fe/Pt_s defined as moles of added $FeCl_2$ per moles of exposed Pt atoms.

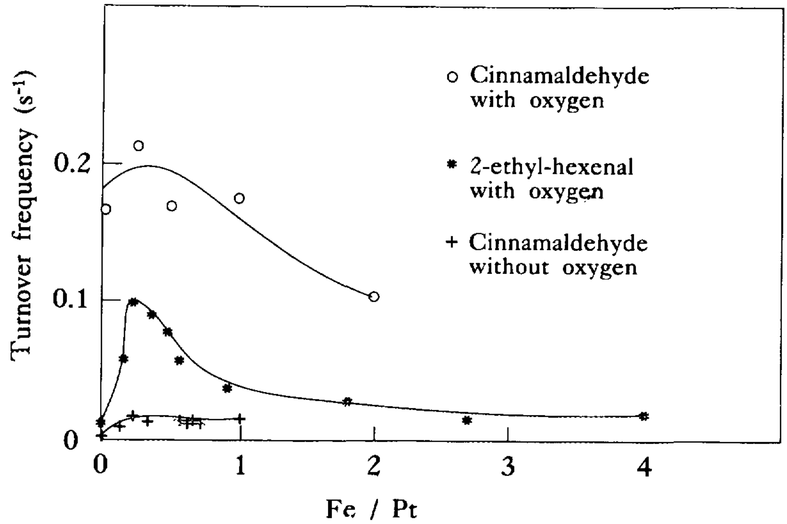

FIG. 2. Turnover frequency at 20% conversion vs Fe/Pt$_s$ for hydrogenation of: (○) 5 ml cinnamaldehyde with oxygen present, T = 333 K, O_2/H_2 = 0.64%; (*) 5 ml 2-ethyl-hexenal with oxygen present, T = 323 K, O_2/H_2 = 0.64%; (+) 5 ml cinnamaldehyde without oxygen present, T = 333 K. Solvent: 0.5 liter ethanol, P_{H_2} = 4 atm, 10 g Pt/Al_2O_3; Fe/Pt$_s$ defined as moles of added $FeCl_2$ per moles of exposed Pt atoms.

bond, giving a higher yield of the saturated aldehyde. The selectivity was switched back toward hydrogenation of the C=O bond by the addition of $FeCl_2$. As in the hydrogenation of 2-ethyl-hexenal over Pt/Al_2O_3, a high activity and selectivity toward the unsaturated alcohol was achieved by the addition of both $FeCl_2$ and oxygen. At higher Fe/Pt$_s$ ratios, the rate decreased but the selectivity for hydrogenation of the C=O to the unsaturated alcohol increased. Some ethyl-benzene and propyl-benzene were also produced. The results are presented in Figs. 2, 4, and 5.

Hydrogenation of 2-Ethyl-hexenal over Pd/Al_2O_3

The hydrogenation rate of 2-ethyl-hexenal on Pd/Al_2O_3 was very high, with an apparent turnover frequency of more than 0.75 s^{-1}. It is likely that the rate here was controlled by the mass transfer. All of the unsaturated aldehyde had been converted to the saturated aldehyde as the first sample was taken (after 5 min). After the unsaturated aldehyde was consumed, the further hydrogenation of the C=O double bond to the saturated alcohol proceeded at a very low rate, which was somewhat increased by the addition of $FeCl_2$. The turnover frequency for the hydrogenation of the saturated aldehyde to the saturated alcohol was 1.2×10^{-4} s^{-1} without iron, and 2.9×10^{-4} s^{-1} with Fe/Pd$_s$ = 1. No unsaturated alcohol was observed over the Pd/Al_2O_3 catalyst.

Hydrogenation of Cinnamaldehyde over Pd/Al_2O_3

Although the hydrogenation rate of the C=C double bond in cinnamaldehyde on Pd/Al_2O_3 was not as fast as that for 2-ethyl-hexenal, it was still very fast in both the presence and absence of $FeCl_2$ (TOF = 0.55 s^{-1} for both Fe/Pd$_s$ = 0 and Fe/Pd$_s$ = 1). The further hydrogenation of the C=O bond to the saturated alcohol was very slow, but was somewhat increased by the addition of $FeCl_2$. Without $FeCl_2$ the turnover frequency of the C=O bond was 3.8×10^{-4}

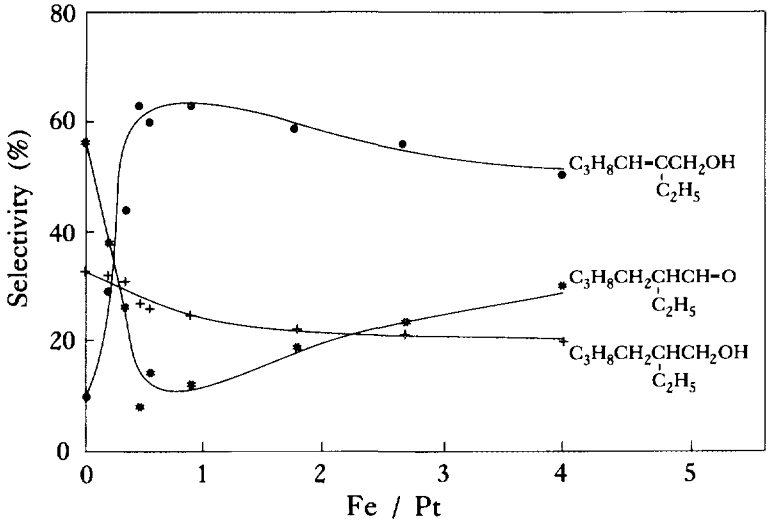

FIG. 3. Selectivities at 20% conversion vs Fe/Pt$_s$ for hydrogenation of 5 ml 2-ethyl-hexenal with oxygen present over 10 g Pt/Al$_2$O$_3$. T = 323 K, P_{H_2} = 4 atm, O$_2$/H$_2$ = 0.64%. Solvent: 0.5 liter ethanol; Fe/Pt$_s$ defined as moles of added FeCl$_2$ per moles of exposed Pt atoms.

s^{-1} and with Fe$_s$/Pd = 1 it was $5 \times 10^{-4}\ s^{-1}$. As in the hydrogenation of 2-ethyl-hexenal over Pd/Al$_2$O$_3$, no unsaturated alcohol was observed.

DISCUSSION

Hydrogenation without Oxygen and Iron

An unmodified platinum catalyst deactivates very fast when it is used for hydrogenation of α,β-unsaturated aldehydes in the absence of oxygen. The reason for this is probably that CO is produced when the aldehyde is decarbonylated in a side reaction (*9*). Decarbonylation of cinnamaldehyde yields ethyl-benzene and decarbonylation of 2-ethyl-hexenal, heptane. Ethyl-benzene was found in the products but heptane could not be observed due to its high volatility. Heptane has, however, been found in the gas-phase hydrogenation of 2-ethyl-hexenal on a platinum catalyst (*9*).

The selectivities for the aldehydes studied are quite different. Cinnamaldehyde is hydrogenated to the saturated alcohol via both the unsaturated alcohol and the saturated aldehyde, whereas 2-ethyl-hexenal is hydrogenated mainly via the saturated aldehyde.

What differentiates the two aldehydes is that all the carbon atoms in the cinnamaldehyde are sp^2 hybridized and belong to the conjugated system. This means that cinnamaldehyde is a rigid, two-dimensional molecule. Moreover, as pointed out by Giroir-Fendler *et al.* (*10*), there is a repulsive force between the metal surface and the phenyl group which hinders its adsorption. This repulsive force together with the rigidity of cinnamaldehyde will make the adsorption of the C=C bond inside the molecule sterically hindered on a flat surface, explaining the structure sensitivity found by Giroir-Fendler *et al.* (*10*). They found that the selectivity toward the unsaturated alcohol decreased when the platinum dispersion increased.

On the other hand, 2-ethyl-hexenal is more flexible and does not have a repulsive phenyl group. This would favor the adsorption and hydrogenation of the C=C double bond, leading to high selectivity for the saturated aldehyde.

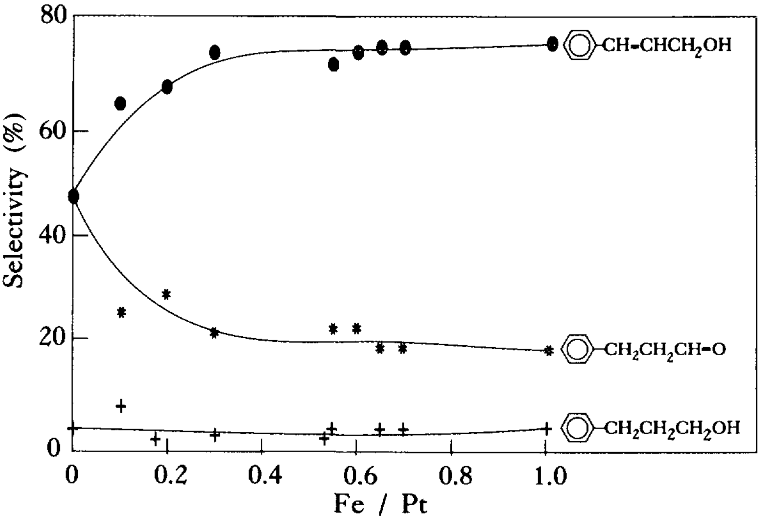

FIG. 4. Selectivities at 20% conversion vs Fe/Pt$_s$ for hydrogenation of 5 ml cinnamaldehyde without oxygen present over 10 g Pt/Al$_2$O$_3$. T = 333 K, P_{H_2} = 4 atm. Solvent: 0.5 liter ethanol; Fe/Pt$_s$ defined as moles of added FeCl$_2$ per moles of exposed Pt atoms.

Besides the geometric difference between cinnamaldehyde and 2-ethyl-hexenal, their electronic properties are different. The phenyl group is a more electron-withdrawing group than the alkyl group. This difference may also affect the selectivities and the activity.

In contrast to the platinum catalyst, both of the α,β-unsaturated aldehydes were hydrogenated to the saturated aldehydes very

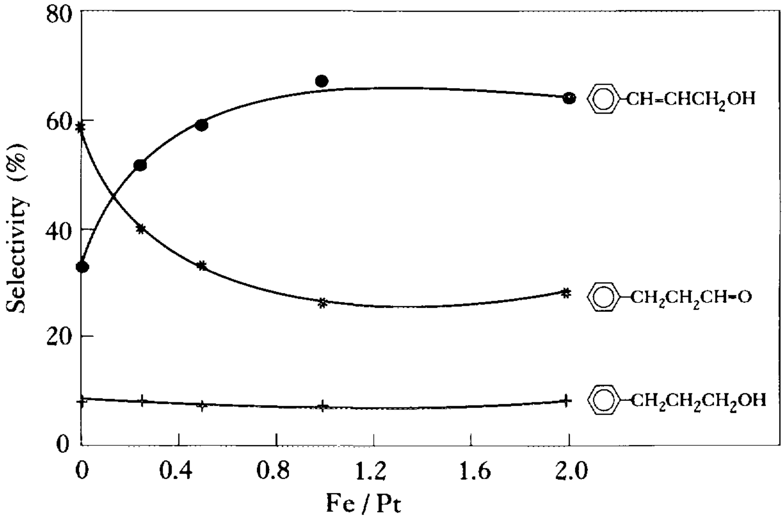

FIG. 5. Selectivities at 20% conversion vs Fe/Pt$_s$ for hydrogenation of 5 ml cinnamaldehyde with oxygen present over 10 g Pt/Al$_2$O$_3$. T = 333 K. P_{H_2} = 4 atm, O$_2$/H$_2$ = 0.64%. Solvent: 0.5 liter ethanol; Fe/Pt$_s$ defined as moles of added FeCl$_2$ per moles of exposed Pt atoms.

quickly over the Pd/Al_2O_3 catalyst. The high rates are consistent with the fact that the aldehydes are not decarbonylated on palladium. The further hydrogenation of the C═O bonds to the saturated alcohols is extremely slow. It seems that palladium in the presence of hydrogen does not adsorb the carbonyl group. Over the Pd/Al_2O_3 catalyst, the hydrogenation rate of 2-ethyl-hexenal is somewhat higher than for cinnamaldehyde. This could be explained by the reduced availability of the C═C group in cinnamaldehyde or by an electronic effect as described above.

Addition of Oxygen

The addition of small amounts of oxygen greatly increases the activity of pure as well as $FeCl_2$-promoted platinum catalyst. The explanation for this is probably that CO_2 is produced, instead of CO, when the aldehyde is decarbonylated (9). It is also very interesting to note that the selectivity for the hydrogenation of cinnamaldehyde is changed by the addition of oxygen. The selectivity is shifted toward hydrogenation of the C═C double bond, yielding more of the saturated aldehyde. One explanation for this could be that oxygen restores sites that are more active for C═C double bond hydrogenation. These sites are probably the edge sites, which are also the most active ones for the decarbonylation reaction ($R\text{–}CH{=}O \rightarrow R\text{–}H + CO$). As a result of this, one would imagine that these edge sites are poisoned by CO to a high degree when no oxygen is present. The addition of oxygen would restore these sites by oxidative removal of CO. The electronic properties of the platinum catalyst may also be changed by the presence of oxygen, and this might also influence the selectivity.

The selectivity for the hydrogenation of 2-ethyl-hexenal was not significantly changed by the addition of oxygen. This is not surprising. In contrast to cinnamaldehyde, the selectivity to the saturated aldehyde is also very high without oxygen.

The effect of oxygen in hydrogenation with a palladium catalyst was not examined in this work. Earlier experiments, however, have shown that the rate of the gas-phase hydrogenation of 2-ethyl-hexenal on palladium was not increased by the presence of oxygen (9). This is also consistent with the fact that no decarbonylation occurs on palladium.

The Effect of Iron

The addition of $FeCl_2$ to the platinum catalyst increased the selectivity toward hydrogenation of the C═O double bond yielding the unsaturated alcohol. The activity also increased for the hydrogenation of cinnamaldehyde in the absence of oxygen at moderate iron concentrations. However, addition of $FeCl_2$ did not prevent the deactivation. Without oxygen, the activity was still low, especially for the hydrogenation of 2-ethyl-hexenal. The reason for the lower hydrogenation rate of 2-ethyl-hexenal could be that decarbonylation of 2-ethyl-hexenal is easier than for cinnamaldehyde, or that the two aldehydes have different electronic properties.

As noted above, measurement of the iron concentration in the solution before the aldehyde was added showed that some iron was adsorbed on the catalyst, and a separate experiment without H_2 showed that the adsorption rate was somewhat higher in the presence of hydrogen. This suggests that some of the added $FeCl_2$ is reduced on the platinum crystallites.

Different explanations for the effect of iron have been proposed. Hotta and Kubomatsu (*11*) examined the effect of iron on a cobalt catalyst. They suggest that the effect is due to a lesser amount of strongly adsorbed hydrogen. This hydrogen is believed to react more easily with the C═C double bond. Another explanation has been proposed by Beccat *et al.* (*5*), who examined the hydrogenation of unsaturated aldehydes on a platinum iron alloy. They suggest that the effect is caused by a change in the geometric and electronic properties of some platinum atoms. The most common explanation, however, is that iron deposed on the catalyst acts as an adsorption site for the carbonyl group (*4*). This makes the adsorption and hydrogenation of the carbonyl group easier.

As more iron is deposited on the catalyst, the platinum surface free for hydrogen adsorption becomes smaller. This could explain why the activity decreases at higher iron concentrations.

At high $FeCl_2$ concentrations, two kinds of acetals were produced. Separate experiments without any Pt catalyst showed that the acetals were products of a reaction between aldehydes and ethanol, catalyzed by $FeCl_2$. The acetals disappear when the aldehydes are consumed. The explanation for this is that the acetal reaction is reversible.

CONCLUSIONS

Pure as well as $FeCl_2$-promoted Pt/Al_2O_3 catalyst deactivated fast when used for hydrogenation of the aldehydes in the absence of oxygen. The deactivation was probably caused by CO produced in a side reaction, decarbonylation of the aldehydes. Addition of small amounts of oxygen prevented the deactivation. In the presence of oxygen, CO_2 is produced instead of CO.

In the absence of oxygen and $FeCl_2$, 2-ethyl-hexenal was hydrogenated mainly via the C=C double bond to yield the saturated aldehyde as intermediate, whereas cinnamaldehyde was hydrogenated via both the C=C and the C=O double bond to give equal amounts of the intermediates, the unsaturated alcohol and the saturated aldehyde.

Addition of oxygen changed the selectivity for cinnamaldehyde but not for 2-ethylhexenal. The hydrogenation rate of the C=C double bond of cinnamaldehyde was increased by the presence of oxygen, which led to a higher yield of the saturated aldehyde.

Addition of $FeCl_2$ increased the activity and the selectivity for hydrogenation of the C=O bond in both 2-ethyl-hexenal and cinnamaldehyde. High yields of the unsaturated alcohols were obtained with Pt/Al_2O_3 in the presence of both $FeCl_2$ and oxygen. $FeCl_2$ was adsorbed on the catalyst and some iron was probably reduced by hydrogen on the platinum crystallites.

The Pd/Al_2O_3 catalyst was very active for hydrogenation of the C=C double bond to the saturated aldehyde. The further hydrogenation of the C=O double bond to the saturated alcohol was very slow, but was somewhat increased by the presence of $FeCl_2$.

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