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Influence of Oxygen in the Gas-Phase Hydrogenation of 2-Ethyl-Hexenal

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The influence of oxygen in the feed on the very fast deactivation of a Pt/Al_2O_3 catalyst during gas-phase hydrogenation of the unsaturated aldehyde, 2-ethyl-hexenal, was investigated (50–160°C, $P = 1$ atm). The addition of oxygen (<0.5%) prevented deactivation and the products obtained were saturated aldehyde, saturated alcohol, deoxygenated aldehyde, and in a side reaction CO_2 and heptane. In the absence of oxygen, the simultaneous H_2–D_2 exchange reaction was inhibited, and the products were saturated aldehyde, saturated alcohol, and in a side reaction CO and heptane. A tested Rh/Al_2O_3 catalyst was deactivated quickly like Pt/Al_2O_3 and the addition of oxygen restored the activity, while the tested Pd/Al_2O_3 and Ru/Al_2O_3 catalysts were not found to deactivate quickly and the addition of oxygen did not increase the activity. The fast deactivation on Pt/Al_2O_3 and Rh/Al_2O_3 might be explained by a side reaction producing CO (R—CH=O → R—H + CO) and the reactivating effect of oxygen addition might be explained by CO_2 produced instead of CO in the side reaction.

INTRODUCTION

In hydrogenation reactions the activities of the working and the fresh catalyst are usually very different. The catalyst often deactivates due to poisons present in the feed or produced in side reactions. It has been found that oxygen in the feed can in some cases prevent deactivation and even result in a higher reaction rate (*1*, *2*). In 1925 Tuley and Adams (*3*) had already found that a mixture of platinum-oxide and platinum black was deactivated when used for aldehyde hydrogenation, and that shaking the reaction mixture with air restored the activity. The deactivation of Pt catalysts in aldehyde hydrogenations may also be prevented by using promoters such as Fe^{2+} (*3*, *4*) and Sn^{2+} (*5*, *6*) or by supporting Pt on TiO_2 (*7*).

Many explanations for the effect of oxygen have been proposed for different catalytic hydrogenations. A common explanation is that the poison on the surface is simply removed by oxidation. Another explanation, proposed by Amariglio *et al.* (*1*, *2*), is that the H_2–O_2 reaction reconstructs the surface and thereby creates new sites with other properties. They found that ethylene hydrogenation on Rh, Co, and Ni were facilitated by oxygen traces in the feed. On a highly dispersed Au/SiO_2 catalyst, Naito and Tanimoto (*8*) showed that the hydrogenation rate of propylene was increased by the addition of small amounts of oxygen. Peroxides on the surface that make the hydrogen dissociation easier were suggested, based on the fact that the H_2–D_2 exchange reaction was also increased. Oxygen could also affect the catalyst by changing the electronic properties of the active metal. Somorjai and co-workers (*9*, *10*) have found that preadsorbed, strongly bound oxygen can increase the hydrogenation rate of cyclohexene on different platinum surfaces and that this probably is due to an electronic structure alteration of platinum.

In this work we have studied the deactivation of a Pt/Al_2O_3 catalyst used for aldehyde hydrogenation and the reactivating effect of oxygen addition to this system. Pt/Al_2O_3,

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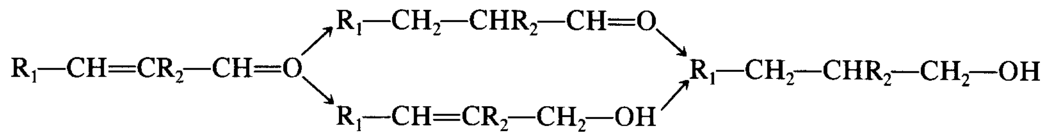
which is an excellent catalyst for hydrogenation of olefins, deactivates very fast when used for aldehyde hydrogenations in the absence of oxygen traces. To explain the behavior of the Pt/Al_2O_3 catalyst we have also compared the effect of oxygen addition on some other common hydrogenation catalysts, i.e., Pd, Rh, and Ru. The aldehyde that has been studied is an α, β-unsaturated aldehyde, 2-ethyl-hexenal. This aldehyde is industrially hydrogenated to the saturated aldehyde and alcohol, the former being used for production of octanic acid and the latter for production of di-octyl-phtalat which is a plastic softener. The reaction to the saturated alcohol can proceed through the saturated aldehyde or the unsaturated alcohol according to



$$\begin{array}{ccccc} & \nearrow & R_1{-}CH_2{-}CHR_2{-}CH{=}O & \searrow & \\ R_1{-}CH{=}CR_2{-}CH{=}O & & & & R_1{-}CH_2{-}CHR_2{-}CH_2{-}OH \\ & \searrow & R_1{-}CH{=}CR_2{-}CH_2{-}OH & \nearrow & \end{array}$$

EXPERIMENTAL

All experiments were carried out under atmospheric pressure with an overall flow rate of 2 ml/s. Hydrocarbon reactants were introduced into the reactor by bubbling N_2 as a diluent gas through a heated evaporator. The partial pressures were: hydrocarbon, ≈ 0.4 kPa; H_2, 6–44 kPa; O_2, 0–0.44 kPa; and the investigated temperature range was 50–300°C. In order to ensure steady state conditions after any change in the reaction conditions, all hydrogenations were performed during a period of about 3 h.

Reactor. The continuous gas-phase hydrogenations were performed in a stainless-steel tube reactor (θ = 3 mm, L = 10 cm) packed with 0.5 g of ⅛-in. catalyst pellets.

Catalysts. Four commercial catalysts were used (Aldrich). These were γ-alumina-supported Pt, Rh, Pd, and Ru, all with the active metal deposed in the outer shell of the ⅛-in. catalysts pellets. The metal contents were determined by atomic absorption spectrometry (Varian spectrAA-10), and the metal dispersions of the catalysts were determined by volumetric chemisorption of hydrogen (Chemisorb 2800), and the surface areas were determined by nitrogen adsorption (Digisorb 2600). The data are given in Table 1.

Analyses. A gas chromatograph (Varian 3300) supplied with a capillary column (30 m × 0.319 mm DB-5) was used for the analyses of the hydrocarbons. Samples were analyzed every 10 min. H_2, D_2, HD, CO_2, and H_2O were continuously measured with a quadrupole mass spectrometer (Balzers QMG 311), while CO was continuously measured with an IR gas analyzer (UNIOR 6N).

RESULTS

Hydrogenation of 2-Ethyl-Hexenal on Pt/Al_2O_3

The effect of oxygen. The experiments showed that the addition of small amounts of oxygen in the feed substantially increased the hydrogenation rate of 2-ethyl-hexenal on Pt/Al_2O_3. At a low temperature (55°C) the unsaturated aldehyde was mainly reduced

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
Rh/Al_2O_3	0.5	104.9	0.75
Pd/Al_2O_3	0.5	82.1	0.64
Ru/Al_2O_3	0.5	100.6	0.22

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

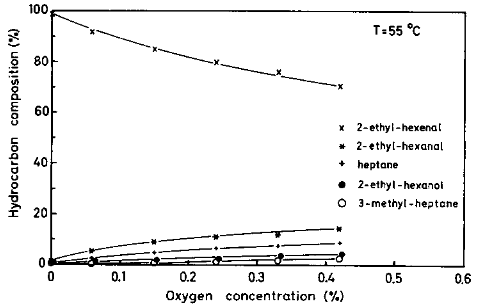


FIG. 1. Effect of oxygen on gas-phase hydrogenation of 2-ethyl-hexenal on Pt/Al_2O_3 at $T = 55°C$. Exposed Pt atoms = 6.1×10^{-6} mol, hydrocarbon flow = 2.8×10^{-7} mol/s, $P = 1$ atm. Feed composition was $H_2 = 20\%$, hydrocarbon = 0.36%, $N_2 = 79.6\%$.

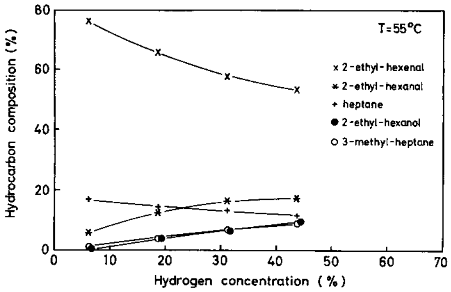


FIG. 3. Effect of hydrogen pressure on gas-phase hydrogenation of 2-ethyl-hexenal on Pt/Al_2O_3 with 0.12% oxygen in the feed at $T = 55°C$. Exposed Pt atoms = 6.1×10^{-6} mol, hydrocarbon flow = 2.8×10^{-7} mol/s, overall flow = 1.1×10^{-4} mol/s, $P = 1$ atm.

to the saturated aldehyde with a lower amount of the saturated alcohol. Besides the reduction of 2-ethyl-hexenal, a large amount of the aldehyde was decomposed to heptane and small amounts of 3-methyl-heptane. Figure 1 shows the hydrocarbon composition in the outlet of the reactor as a function of the oxygen concentration. At a higher temperature (115°C) the main product was heptane and the amount increased with oxygen concentration, as shown in Fig. 2. Addition of oxygen also resulted in the production of water and carbon dioxide.

The effect of hydrogen pressure. The influence of the hydrogen pressure on the hydrogenation of 2-ethyl-hexenal on Pt/Al_2O_3 was further investigated at a constant oxygen concentration. Figure 3 shows that except for the heptane yield, all product yields were increased at higher hydrogen pressure.

The effect of temperature. In the absence of oxygen, Pt/Al_2O_3 was not able to reduce the unsaturated aldehyde at temperatures below 80°C. At higher temperatures, however, reactions took place that also produced CO and heptane in equal amounts, in addition to the saturated aldehyde and the saturated alcohol. The influence of the temperature is shown in Fig. 4.

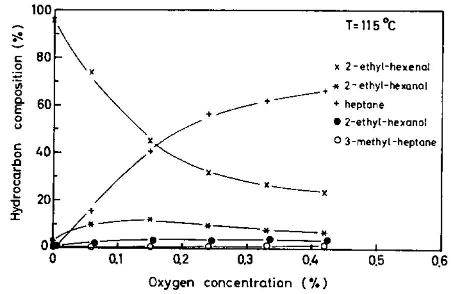


FIG. 2. Effect of oxygen on gas-phase hydrogenation of 2-ethyl-hexenal on Pt/Al_2O_3 at $T = 115°C$. Exposed Pt atoms = 6.1×10^{-6} mol, hydrocarbon flow = 2.8×10^{-7} mol/s, $P = 1$ atm. Feed composition was $H_2 = 20\%$, hydrocarbon = 0.36%, $N_2 = 79.6\%$.

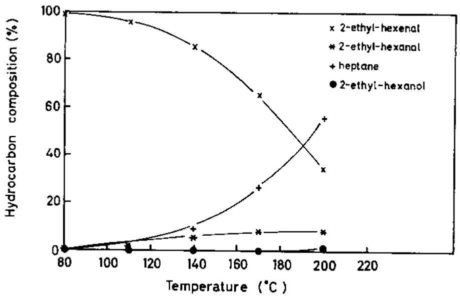


FIG. 4. Effect of temperature on gas-phase hydrogenation of 2-ethyl-hexenal on Pt/Al_2O_3 in the absence of oxygen. Exposed Pt atoms = 6.1×10^{-6} mol, hydrocarbon flow = 2.8×10^{-7} mol/s, $P = 1$ atm. Feed composition was $H_2 = 20\%$, hydrocarbon = 0.36%, $N_2 = 79.6\%$.

The effect on the H_2–D_2 exchange. Measurement of the HD yield from the H_2–D_2 exchange reaction showed that 2-ethyl-hexenal prevented HD formation on Pt/Al_2O_3 at low temperature and in the absence of oxygen. However, addition of oxygen to the feed resulted in an increase in the HD formation again, as shown in Fig. 5. Interesting to note is that the carbon dioxide production showed a maximum just after oxygen was added, and that the water production slowly increased when oxygen was added (Fig. 5). Addition of oxygen to a clean Pt/Al_2O_3 catalyst did not affect the H_2/D_2 reaction. This experiment was performed at high space velocity with the $H_2/D_2/HD$ reaction far from equilibrium.

Hydrogenation of 2-Ethyl-Hexanal on Pt/Al_2O_3

The hydrogenation of the corresponding saturated aldehyde, 2-ethyl-hexanal, on Pt/Al_2O_3, was also investigated. The hydrogenation of the saturated aldehyde behaved much like the hydrogenation of the unsaturated aldehyde. Addition of oxygen increased the rate of both the reduction and the decomposition of the aldehyde. However, in contrast to the unsaturated aldehyde, the saturated aldehyde decomposed to a greater extent by breakage of the C=O bond, resulting in the formation of 3-methyl-heptane. Figure 6 shows the influence of oxygen concentration at 55°C.

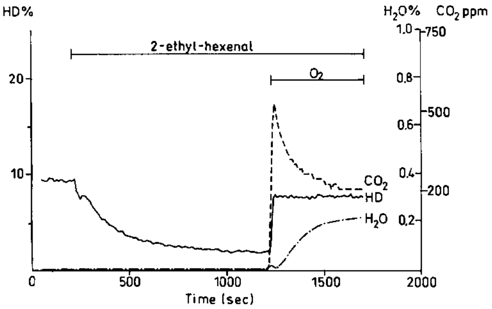


FIG. 5. Production of HD, CO_2, and H_2O when 2-ethyl-hexenal (0.36%) and oxygen (0.4%) are added to Pt/Al_2O_3. Initial feed composition was H_2 = 10%, D_2 = 10%, N_2 = 80%. T = 70°C, P = 1 atm, exposed Pt atoms = 6.1×10^{-6} mol, overall flow = $6.8 = 10^{-5}$ mol/s.

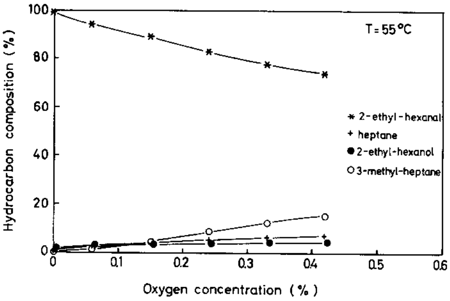


FIG. 6. Effect of oxygen on gas-phase hydrogenation of 2-ethyl-hexanal on Pt/Al_2O_3 at T = 55°C. Exposed Pt atoms = 6.1×10^{-6} mol, hydrocarbon flow = 4.4 $\times 10^{-7}$ mol/s, P = 1 atm. Feed composition was H_2 = 20%, hydrocarbon = 0.57%, N_2 = 79.4%.

H_2–D_2 experiments showed that the saturated aldehyde, like the unsaturated, inhibited the HD formation and that the addition of oxygen counteracted this inhibition.

Hydrogenation of Some Other Hydrocarbons on Pt/Al_2O_3

The influence on the H_2/D_2 reaction on Pt/Al_2O_3 was also studied for some other hydrocarbons. These were 2-ethyl-hexanol, decene, and methyl-iso-butyl-ketone. None of these led to a decrease in the HD yield as in the case of the aldehydes. Decene was, in contrast to 3-methyl-ketone, readily hydrogenated.

Hydrogenation of 2-Ethyl-Hexenal on Some Other Catalysts

The effects of O_2 on hydrogenation of 2-ethyl-hexenal on Rh/Al_2O_3, Ru/Al_2O_3, and Pd/Al_2O_3 were also investigated. Rh/Al_2O_3 like Pt/Al_2O_3 showed very low activity without O_2 for hydrogenation of the unsaturated aldehyde (55–100°C). Addition of oxygen increased the activity. In contrast to Pt/Al_2O_3, however, the saturated alcohol and 3-methyl-heptane were not observed. For Ru/Al_2O_3 a higher temperature ($T > 100$°C) was required to obtain reactions. The products were the saturated aldehyde, heptane, and small amounts of the alcohol. Addition of oxygen led to a decrease in the saturated aldehyde yield and an increase in the heptane yield. The heptane yield increased with temperature and the production of the saturated aldehyde showed a maximum at 130°C. Pd/Al_2O_3, however, was very active and selective for the reduction of the unsaturated to the saturated aldehyde, and the HD formation was not inhibited during the hydrogenation.

DISCUSSION

Deactivation of Pt/Al_2O_3

Hydrogenation of saturated and unsaturated aliphatic aldehydes on Pt/Al_2O_3 is self-poisoned at low temperatures. The reason for this seems to be that some of the aldehydes are decomposed into CO and the corresponding alkane (R—CH=O → R—H + CO). The aldehydes also inhibit dissociative hydrogen adsorption as shown by the decrease in the rate of H_2/D_2 exchange. With the ketone, however, no poisoning effect on H_2/D_2 exchange was found. This is probably due to the fact that the decarbonylation rate is much slower for the ketone. If the carbonyl group in the aldehyde were responsible for the poisoning, then the ketone would probably also give some poisoning.

The Effect of Oxygen on Pt/Al_2O_3

Addition of traces of oxygen (<1%) in the feed to the poisoned catalyst increases the H_2/D_2 exchange rate and the reaction rates of both the hydrogenation and the decomposition of the aldehyde. With oxygen in the feed CO_2 is produced instead of CO. Whether oxygen reacts with an intermediary in the decarbonylation reaction or whether oxygen reacts with carbon monoxide already produced from the decarbonylation reaction is not yet clear. In transient experiments when oxygen is added in the feed to an already poisoned catalyst, there is a peak in CO_2 production, indicating that oxygen reacts with a compound accumulated on the surface.

Although it seems that the main effect of O_2 in our case is to clean the poisoned sites, it is probable that O_2 can also affect the catalyst in other ways. This is supported by the deoxygenation that occurs only when O_2 is present. McCabe and Schmidt (*11*) found that CO and H_2 were more strongly bound to a Pt(110) surface when the surface was oxidized and that the sticking coefficient was increased for H_2 but decreased somewhat for CO. They suggested three models to explain this effect: "microfaceting," electronic structure alteration, and compound formation. Davis and Somorjai (*12*) found that the hydrogenation rate for cyclohexene increased when the surfaces were partly covered with strongly bound oxygen. They explained this with an electronic structure alteration. In our experiments we probably did not have this unreactive oxygen since our catalyst had not been exposed to oxygen at high temperatures and the catalyst deactivated fast when the oxygen was removed from the feed. However, an electronic structure alteration may explain the deoxygenation of the aldehyde (R—CH=O → R—CH_3).

Amariglio and Amariglio (*1*) showed that traces of O_2 increased activity for ethylene hydrogenation on Rh ribbons. Their explanation was that the H_2–O_2 reaction changed the surface structure and thereby created new sites. Oxygen has also been shown to increase activity for propylene hydrogenation and HD formation on a highly dispersed Au catalyst (*8*). Oxygen is believed to be in a "preoxo"-like adsorbed state, which increases hydrogen dissociation. On Pt/Al_2O_3, however, addition of O_2 without the presence of the aldehydes did not lead to a higher HD yield. Here the most probable explanation is that O_2 helps in cleaning the poisoned sites for hydrogen adsorption.

The Hydrogenation on Rh, Ru, Pd, and Ni Catalysts

Of the other catalysts tested, rhodium is very similar to platinum. They are both excellent catalysts for olefinic reduction and poor catalysts for reduction of the unsaturated aldehyde. The catalyst deactivates fast and decarbonylation occurs readily. Addition of oxygen does increase the reaction rate. On Ni the unsaturated aldehyde is readily hydrogenated to the saturated aldehyde and then further hydrogenated to the saturated alcohol. Some decarbonylation occurs especially on a fresh catalyst. Pd is a very selective catalyst for the reduction of the unsaturated aldehyde. The reaction stops at the saturated aldehyde and no decarbonylation occur. Addition of oxygen does not affect the selectivity while the activity is decreased somewhat. This is probably due to consumption of hydrogen by the oxygen.

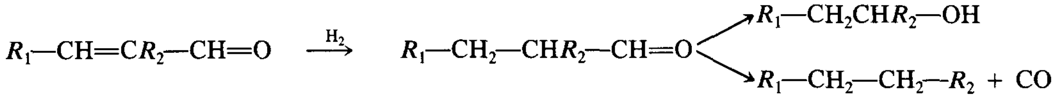
The poor activities with Pt and Rh could be explained by the side reaction that produces CO and heptane, and the improvement with oxygen could be explained by the CO_2 produced instead of CO. The relatively good activity of Ni in spite of the fact that some of the aldehyde is decomposed is more difficult to explain. It is possible that the decomposition rate to heptane and carbon monoxide is not sufficiently high to cause a complete poisoning of the Ni catalyst. Palladium, on the other hand, does not decompose the aldehyde. The reduction rate of the olefinic bond is indeed very high, and addition of oxygen does not increase the rate. Ruthenium, which is known as one of the best catalysts for the reduction of C=O bonds and one of the slowest for C=C bonds, showed low activity for the hydrogenation of the unsaturated aldehyde. The low activity is probably due to the fact that the C=C bond must be reduced before the C=O bond. This is in agreement with the results by Rylander *et al.* (*4*) who found that the alkene was reduced first in a mixture with an aldehyde. Oxygen did not increase the hydrogenation rate on ruthenium probably because of another reason for the low activity.

CONCLUSIONS

Pt/Al_2O_3 and Rh/Al_2O_3 are poor catalysts for hydrogenation of aliphatic aldehydes (2-ethyl-hexenal, 2-ethyl-hexanal). The most likely reason for this is that the hydrogen adsorption is prevented when some of the aldehyde is decomposed into alkanes and CO on these catalysts.

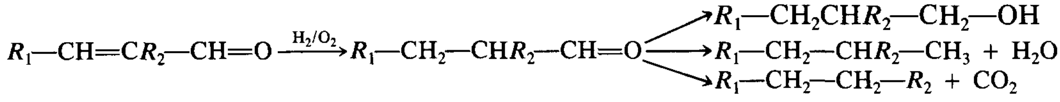
Addition of oxygen to the feed leads to an increase of the reaction rate for both the hydrogenation and the decarbonylation of the aldehyde. Oxygen is considered to reactively remove the species that block the sites for hydrogen adsorption, and CO_2 is produced instead of CO.

The reaction paths for 2-ethyl-hexenal are



$$R_1\text{—CH=C}R_2\text{—CH=O} \xrightarrow{H_2} R_1\text{—CH}_2\text{—CH}R_2\text{—CH=O} \begin{cases} \nearrow R_1\text{—CH}_2\text{CH}R_2\text{—OH} \\ \searrow R_1\text{—CH}_2\text{—CH}_2\text{—}R_2 + \text{CO} \end{cases}$$

without traces of oxygen, and



$$R_1\text{—CH=C}R_2\text{—CH=O} \xrightarrow{H_2/O_2} R_1\text{—CH}_2\text{—CH}R_2\text{—CH=O} \begin{cases} \nearrow R_1\text{—CH}_2\text{CH}R_2\text{—CH}_2\text{—OH} \\ \rightarrow R_1\text{—CH}_2\text{—CH}R_2\text{—CH}_3 + H_2O \\ \searrow R_1\text{—CH}_2\text{—CH}_2\text{—}R_2 + CO_2 \end{cases}$$

with traces of oxygen.

Deoxygenation of the aldehyde occurs only when oxygen is present in the feed, and no unsaturated alcohol is observed with or without oxygen traces on Pt/Al_2O_3. The hydrogen adsorption is not prevented during the hydrogenations of decene and methyl-iso-butyl-ketone, and the reaction rates are not increased by oxygen. Pd/Al_2O_3 is very active and selective for reduction of the unsaturated to the saturated aldehyde, and traces of oxygen do not increase the reaction rate. Ru/Al_2O_3 requires higher temperature ($T > 100°C$) to get reactions and oxygen does not increase the rate. No alcohol and no 3-methyl-heptane were found.

ACKNOWLEDGMENTS

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