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Selective hydrogenation of acetic acid towards acetaldehyde [a]

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Abstract. As a model reaction for the selective hydrogenation of carboxylic acids towards aldehydes, the reaction of acetic acid towards acetaldehyde has been investigated. Various oxides are used as catalysts, including platinum-enriched oxides. It appeared that oxides with a moderate metal–oxygen bond strength are good catalysts, provided that a source of activated hydrogen is present. On exposure to molecular hydrogen zero-valent metals can produce activated hydrogen. Addition of precious metals, such as Pt, or completely reducing part of the oxidic catalyst can provide the zero-valent metal. The hydrogenation probably occurs on the oxidic surface by a Mars and Van Krevelen type of mechanism.

Introduction

Aldehydes are frequently used intermediates for a large range of chemical processes and a lot of different methods are exploited to produce them[1]. Carboxylic acids are readily available from certain industrial processes or from natural resources and thus one way to produce aldehydes is by the so-called *Rosenmund* reduction of carboxylic acids[2,3]. This is a two-step synthesis that produces a lot of waste. A potential alternative is the direct catalytic hydrogenation of carboxylic acids, but until now this method has only been successful for carboxylic acids with no or at most one α-hydrogen (e.g., benzoic acid)[4–9]. No research has yet been done on the selective catalytic reduction of carboxylic acids having more than one α-hydrogen. Results of explorative research dealing with this problem are presented in this article. The reaction of acetic acid to acetaldehyde has been taken as a model reaction.

In literature, a large number of experiments are described concerning the behaviour of acetic acid on metals and oxides in high vacuum systems[10–17]. Acetic acid can be adsorbed dissociatively to form a surface acetate, which can desorb as acetic acid or decompose further. None of these papers mentions the formation of substantial quantities of acetaldehyde. Only a few investigations were done under higher pressure of acetic acid; such conditions lead to the production of ketene and acetone[18,19].

Surprisingly, none of the above-mentioned experiments were performed in a hydrogen atmosphere. Information concerning the selective catalytic hydrogenation of alkanoic acids towards aldehydes appears to be missing from the literature. Therefore we decided to start with an exploratory study on the behaviour of various oxides. The influence of reduction pretreatment and of the addition of platinum, to facilitate hydrogen dissociation, were also investigated.

Results

Pure oxides

First, a range of oxidic catalysts were tested, using the most oxidized form of the metal. The results are shown in Figure 1. The oxides are placed in order of increasing metal–oxygen bond strength, calculated from the heat of formation per oxygen atom[20,21].

It can be seen that the selectivity is poor at high metal–oxygen bond strength. The most frequently observed byproduct on these oxides was acetone, produced simultaneously with water and carbon dioxide.

As the reactions are performed under reducing conditions and are accompanied by the formation of oxidizing products like water, the valency of the surface metal ions during reaction is not always clear. The influence of pretreatment by reduction was tested for iron oxide; the results are shown in Figure 2. Iron oxide, which is reduced at temperatures of 400°C or lower, shows a poor selectivity for acetaldehyde. However, when the reduction temperature exceeds 400°C a large amount of acetaldehyde is produced. The XRD patterns of the oxides reduced at temperatures below 400°C show only peaks of the oxidic forms of iron (Fe_2O_3 and Fe_3O_4). The catalysts reduced at 450 and 500°C show the coexistence of Fe^0 and Fe^{n+}; above these temperatures only Fe^0 can be detected by XRD.

Tin oxide (with and without platinum) shows a lower selectivity at higher reduction temperatures. This is a reversible process, since re-oxidation (in an oxygen flow at 200°C for 1 h) results in an increased selectivity. These results are presented in Tables I and II.

In order to clarify the possible significance of hydrogen, the carrier gas was switched over from hydrogen to he-

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[a] This paper is dedicated to the 70th birthday of Professor *W.M.H. Sachtler*.

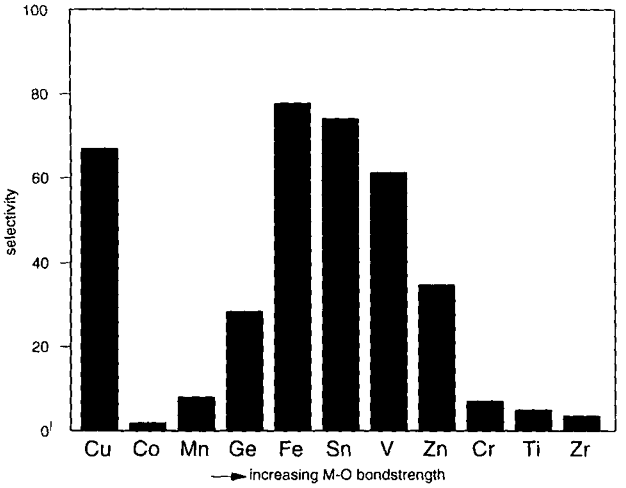


Figure 1. The selectivity towards acetaldehyde of some oxides at the temperature at which the highest activity towards acetaldehyde is found.

lium during the reaction over iron oxide at the constant temperature of 350°C (Figure 3). Under hydrogen, the reaction products were mainly acetaldehyde, after the switch to helium no products were seen initially, later acetone was the main product.

Platinum-enriched oxides

The influence of the addition of platinum to several metal oxides was investigated. Most oxides show an improved selectivity and all show an enhanced activity, but there are clearly some differences in the effect of adding Pt as can be seen in Figure 4.

The iron oxide with platinum added shows almost the same behaviour as iron oxide reduced at 450°C. Tin oxide shows a slight enhancement of the maximum selectivity. Other oxides which produce predominantly acetone, such as those of vanadium, chromium and titanium, cease to form acetone when platinum is added. In these cases other products are produced instead, one of which is acetaldehyde. In Figures 5 and 6 the influence of adding platinum to titanium oxide is shown. It should be stressed that platinum itself does not produce acetaldehyde under the same conditions (Figure 7).

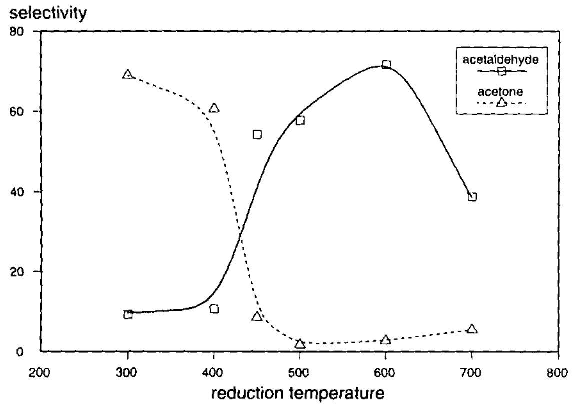


Figure 2. Iron oxide: selectivity towards acetaldehyde and acetone versus reduction temperature (reaction temperature 350°C).

Table I Tin oxide: selectivity towards acetaldehyde at different reduction temperatures (reaction temperature 450°C).

Pretreatment	Selectivity	Yield
reduction 325°C	40	40
reduction 475°C	16	13

Table II Tin-oxide + platinum: selectivity towards acetaldehyde at different reduction temperatures (reaction temperature 300°C).

Pretreatment	Selectivity	Yield
reduction 200°C	87	6.0
reduction 400°C	97	1.8
reduction 475°C	49	1.2
reduction 475°C and oxidation 200°C	96	3.5

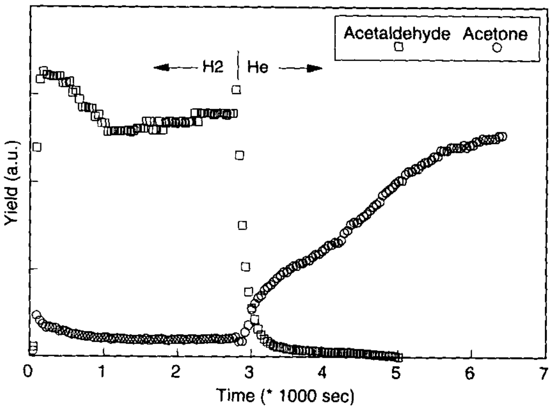


Figure 3. Iron oxide: yields versus time. The carrier gas was changed from hydrogen to helium halfway through the experiment (reaction temperature 350°C)

Germanium oxide behaves in a particularly interesting way, as can be seen in Figures 8 and 9. The pure metal oxide exhibits a poor selectivity and activity, but addition of platinum results in a surprisingly high production of acetaldehyde.

Discussion

Pure oxides

Contrary to previous predictions it is found that the catalytic production of aldehyde from a carboxylic acid which contains α-hydrogen atoms is indeed possible. Clearly, not all oxides behave in the same way. As can be seen in Figure 1 especially oxides having a low metal–

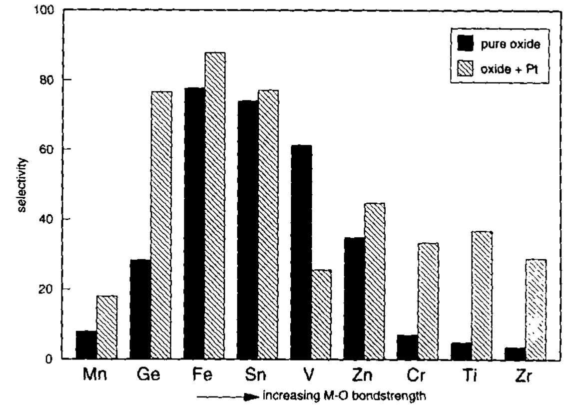


Figure 4. The selectivity towards acetaldehyde of some oxides with and without platinum. The maximum selectivity towards acetaldehyde found is given.

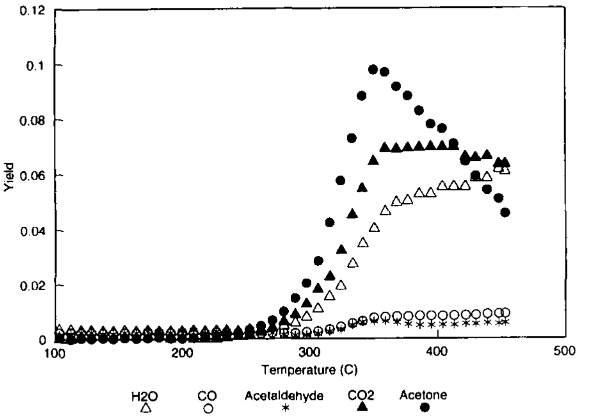


Figure 5. Titanium oxide: yields of all products as a function of temperature.

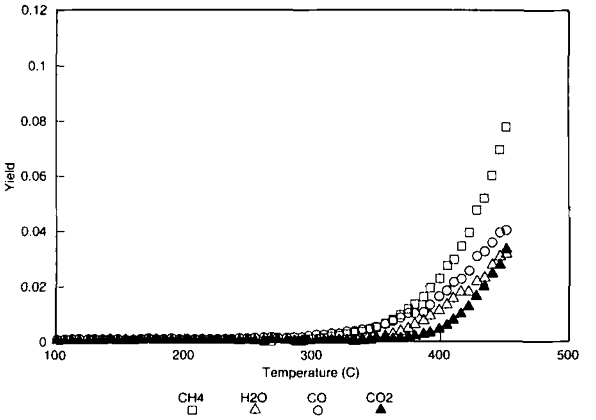


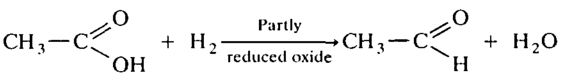
Figure 7. Platinum: yields of all products as a function of temperature.

oxygen bond strength produce acetaldehyde. These oxides are easily reducible and probably can accommodate a lot of defects (oxygen vacancies) under reaction conditions (i.e., in a hydrogen atmosphere at elevated temperatures). In the case of iron oxide (Figure 2) it can be seen that partial reduction of the catalyst is necessary for selective hydrogenation. XRD data show the simultaneous existence of an oxide and a metal. This implies that either partially reduced oxide or completely reduced metal is required for the selective hydrogenation.

It should be noted that, using for example nickel or copper, complete reduction suppresses the desired reaction completely[22]. This is also found for the tin oxide and platinum/tin-oxide catalysts (Tables I and II). The latter catalyst regains its selectivity when a re-oxidation step is performed, emphasising the need for an oxidic phase to be present. So, in order to reach a high selectivity with an originally oxidic catalyst, a partial but not a complete reduction is necessary. On iron, an oxidic layer is, probably, formed by acetic acid decomposition under reaction conditions, even if the most reduced form of iron (Fe^0) is used initially[23]. A Mars and Van Krevelen type of mechanism[24,25], where defects in the lattice accept oxygen from the adsorbent, can be used to explain the experimental results adequately.

The role of hydrogen in the selective hydrogenation to acetaldehyde is two-fold. Hydrogen causes the partial reduction of the catalyst and the reaction towards acetaldehyde consumes stoichiometrically one hydrogen molecule per reacted acetic acid molecule. The instantaneous decline of acetaldehyde production when hydrogen is removed from the gas flow accentuates the need of hydrogen (Figure 3). When hydrogen is replaced by helium, at first no products are seen (possibly because all the acetic acid is initially used to re-oxidise the surface) and later only acetone is produced.

Acetaldehyde is probably produced as described in Scheme 1.



$$CH_3-C\overset{O}{\underset{OH}{\lessgtr}} + H_2 \xrightarrow[\text{reduced oxide}]{\text{Partly}} CH_3-C\overset{O}{\underset{H}{\lessgtr}} + H_2O$$

Scheme 1.

Platinum-enriched oxides

As not every oxide is able to adsorb hydrogen dissociatively to the same extent, differences in activity may also be governed by the capability of each oxide to activate hydrogen. To test this hypothesis, platinum was added to ensure the presence of dissociated hydrogen on the catalyst surface.

The well-reduced iron oxide showed no changes in reaction pattern when platinum was added. But as the XRD results show, a part of this catalyst was already completely reduced to zero-valent iron. So in this case a source of activated hydrogen (Fe^0) is already present in iron catalyst, even without platinum[26,27]. This probably explains why, with iron oxide, hydrogenation activity is only seen above the reduction temperature of 400°C (Figure 4), as below this temperature no Fe^0 is seen by XRD.

The oxides of titanium, vanadium, chromium, zirconium and zinc produce acetone when no platinum is present. By adding platinum, hydrogenated compounds are formed instead of acetone. As one of them is acetaldehyde the selectivity of enriched oxides as given in Figure 4 is increased in comparison to the pure oxides, although it

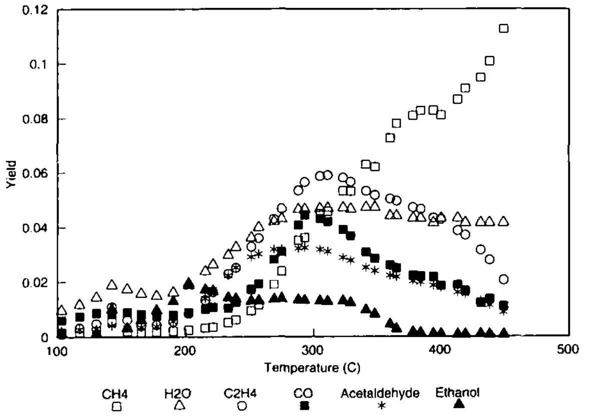


Figure 6. Titanium-oxide + platinum: yields of all products as a function of temperature.

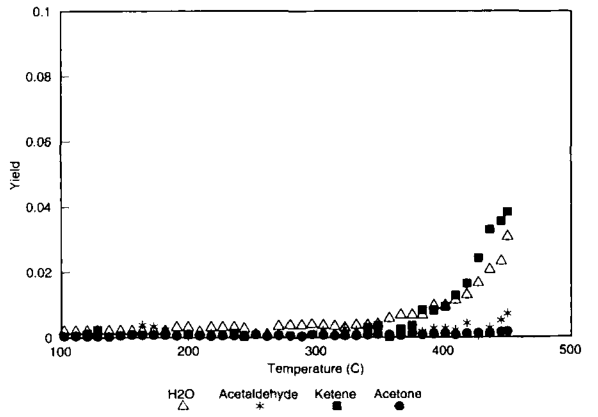


Figure 8. Germanium oxide: yields of all products as a function of temperature.

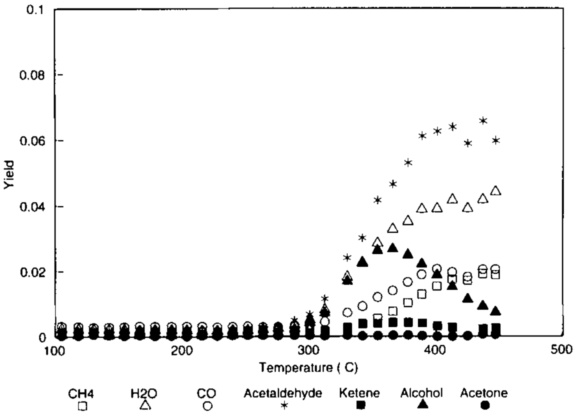


Figure 9. Germanium-oxide + platinum: yields of all products as a function of temperature.

never exceeds 40%. The platinum-activated hydrogen can either enhance the reduction of the oxide or be a reactant in the hydrogenation reaction. One or both of these effects improve acetaldehyde production. However, in the case of zinc and zirconium oxides, platinum-enhanced reduction is very unlikely under these reaction conditions, as these oxides are difficult to reduce. Thus the only effect of platinum is probably to supply one of the reactants (i.e., dissociated hydrogen) for the hydrogenation of carboxylic acid on the catalyst's surface. Nevertheless, oxides with a stronger metal–oxygen bond still remain less selective than the easier reducible catalysts, probably because not enough oxygen vacancies are available.

Special attention should be paid to germanium oxide. This catalyst has roughly the same metal–oxygen bond strength as iron or tin oxide, but has hardly any activity in acetaldehyde formation. When platinum is deposited on germanium oxide, however, the selectivity reaches a value comparable to that of iron oxide. This behaviour can be understood if one considers the fact that a temperature of about 600°C is needed to reduce germanium oxide completely, so with the reaction conditions used, no zero-valent germanium, is present. If platinum is added, a zero-valent metal is present and a source of activated hydrogen is thus available.

An overall picture, describing the selective reduction of acetic acid towards acetaldehyde is depicted as in Figure 10.

Conclusions

It is possible to produce acetaldehyde catalytically from acetic acid with a high selectivity, although acetic acid contains α-hydrogen atoms. In addition to the requirement for a hydrogen atmosphere, the following conditions are needed to produce acetaldehyde:

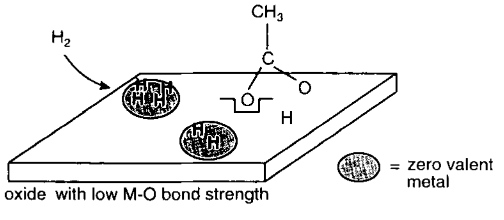


Figure 10. Schematic representation of the possible surface reactions leading to acetaldehyde.

- An oxide with a low metal–oxygen bond strength has to be used as a catalyst.
- Activation of hydrogen by zero-valent metal must occur. Either an added metal (e.g., platinum) or a part of the (originally) oxidic catalyst which is completely reduced can activate hydrogen.

Experimental

The pure oxides were used as purchased, i.e., as powders (SnO_2 and Fe_2O_3: Fluka, Switzerland; V_2O_5, CrO_2, ZnO and Co_3O_4: BDH, England; CuO and ZrO_2: Merck, Germany; MnO_2: Aldrich, USA; TiO_2: Tioxide, England; GeO_2 ex $GeCl_4$: Janssen, The Netherlands). Platinum-added catalysts were prepared by dissolving H_2PtOH_6 (Johnson Matthey, England) in water with as little as possible nitric acid. The oxide was suspended in this solution, followed by evaporation, drying (90°C, overnight), calcination (oxygen flow, 400°C, 5 h) and reduction (hydrogen flow, 300°C, 3 h). The platinum content was 5 at%.

The catalytic experiments were performed in a flow system, working 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 at about 15 Torr) and led over a microreactor containing 0.2 g of catalyst. During the reaction, temperature was raised from room temperature to 450°C at a rate of 7°C/min. Analysis was done quasi-continuously by a mass spectrometer (Balzers QMG 064). The recorded values were corrected for the sensitivities (by the same method as described by *Ko* et al.[28]) and overlapping fragmentation peaks. The appearance of the following products was recorded: methane, carbon monoxide, carbon dioxide, water, ketene, acetone, acetaldehyde, ethanol, ethene and propene.

The selectivity is calculated per carbon atom.

Acknowledgment

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References

[1] *T. Maki* and *T. Yokoyama*, Org. Synth. Chem. **49**, 195 (1991).
[2] "Encyclopedia of Chemical Technology", *R.E. Kirk* and *D.F. Othmer*, eds., Interscience Publishers, N.Y. 1947 p. 351.
[3] *K.W. Rosenmund*, Ber. **51**, 585 (1918).
[4] *T. Maki*, European Patent 0150961 (1985).
[5] *F. Wattimena* and *H.J. Heijman*, European Patent 0101111 (1984).
[6] *N. Ding, J. Kondo, K. Domen, T. Yokoyama, N. Fujita* and *T. Maki*, Cat. Letters **17**, 309 (1993).
[7] *T. Yokoyama, T. Setoyama, N. Fujita, M. Nakajima* and *T. Maki*, Appl. Catal. **A 88**, 149 (1992).
[8] *D.C. Hargis*, U.S. Patent 4950799 (1990).
[9] *P.C. Van Geem* and *L.H.W. Janssen*, European Patent 0290096 (1988).
[10] *J.B. Benziger* and *R.J. Madix*, J. Catal. **65**, 49 (1980).
[11] *X.D. Peng* and *M.A. Barteau*, Cat. Letters **7**, 395 (1990).
[12] *H. Idriss, K.S. Kim* and *M.A. Barteau*, "Structure-, Activity- and Selectivity Relationships in Heterogeneous Catalysis", *R.K. Grasselli* and *A.W. Sleight*, eds., Elsevier, Amsterdam, 1991, p. 327.
[13] *K.S. Kim* and *M.A. Barteau*, J. Catal. **125**, 353 (1990).
[14] *N. Aas* and *M. Bowker*, J. Chem. Soc. Faraday Trans. **89**, 1249 (1993).
[15] *M. Bowker, H. Houghton* and *K.C. Waugh*, J. Catal. **79**, 431 (1983).
[16] *Q. Gao* and *J.C. Hemminger*, J. Electron Spectr. Relat. Phenom. **54/55**, 667 (1990).
[17] *J.J. Vajo, Y.-K. Sun* and *W.H. Weinberg*, J. Phys. Chem. **91**, 1153 (1987).
[18] *D. Kohl, W. Thoren, U. Schnakenberg, G. Schüll* and *G. Heiland*, J. Chem. Soc. Faraday Transactions **87**, 2647 (1991).
[19] *L.M. Parker, D.M. Bibby* and *I.J. Miller*, J. Catal. **129**, 438 (1991).
[20] *I. Komuro, H. Yamamoto* and *T. Kwan*, Bull. Chem. Soc. Japan **36**, 1532 (1963).
[21] *Y. Morooka* and *A. Ozaki*, J. Catal. **5**, 116 (1966).

[22] *R. Pestman*, to be published.

[23] *R. Pestman, E.J. Grootendorst, R.M. Koster* and *V. Ponec*, accepted for publication in J. Catal.

[24] *P. Mars* and *D.W. van Krevelen*, Chem. Eng. Sc. **3**, 41 (1954).

[25] *C. Kröger*, Z. Anorg. Algem. Chem. **206**, 289 (1932).

[26] *G.W.R. Leibbrandt* and *F.H.P.M. Habraken*, J. Catal. **143**, 102 (1993).

[27] *V. Ponec, Z. Knor* and *S. Cerny*, "Adsorption on Solids", Butterworths, London, 1971.

[28] *E.I. Ko, J.B. Benzinger* and *R.J. Madix*, J. Catal. **62**, 264 (1980).