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A Study on the Selectivity in Acrolein Hydrogenation on Platinum Catalysts: A Model for Hydrogenation of α,β-Unsaturated Aldehydes

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Hydrogenation of acrolein, as a model molecule representing the α,β-unsaturated aldehydes, has been studied with SiO_2- and Al_2O_3-supported Pt and Cu catalysts. These catalysts were used to study the effects of various surface modifications. In addition to sulfurization by thiophene, the Pt/SiO_2 catalysts were modified by acetylene, by inactive metal (Sn, Cu) admixture, and by gas modifiers (CO). Furthermore, the effect of modification of the surface by the reaction mixture in the initial stages of the reaction was followed. It appeared that the selectivity in the hydrogenation of the α,β-unsaturated aldehydes is influenced mainly by the presence of sites on the catalysts, which activate the aldehydic oxygen and allow an easy supply of hydrogen atoms. Effect of the ensemble size is much less important. Sulfurization as performed in this paper causes only a marginal effect on selectivity. Small selectivity effects can be also caused by gas modifiers like carbon monoxide.

INTRODUCTION

There is a growing interest in selective hydrogenation of α,β-unsaturated aldehydes over metallic, promoted catalysts, as a selection of papers documents (1–5). Hydrogenation of acrolein is a useful model of these reactions and it is of commercial interest to achieve a high selectivity for allyl alcohol. In spite of all efforts, definitive answers to questions such as which factor determines the desired selectivity for unsaturated alcohols or how the selectivity can be manipulated have not been found yet. The general knowledge is still at the stage of collection of data and ideas which should eventually lead to a rationalized preparation of selective catalysts. Using surface science techniques, information which can serve as a basis for the discussion of the promotion effects on the atomic level has been collected (6, 7).

In this paper, which extends our earlier studies (8), the following aspects of selectivity of the promoted platinum catalysts will be discussed: (i) poisoning of the catalyst surface by sulfur or carbonaceous layer deposition; (ii) self-modification of the catalyst surface by the reaction mixture itself, in particular, when platinum–tin catalysts are used, and (iii) transient poisoning by carbon monoxide pulses. Our previous results (8) and recent papers in the literature [see, e.g., 9–17] offer a basis on which an attempt can be made to explain observations (i)–(iii).

Special attention has been given in this paper to the problem of the effect of sulfurization. In our earlier paper only a very small effect was observed (6), but in some other simultaneously appearing papers a very substantial effect was claimed (17–19). Since the sulfurization techniques applied differed, in this paper we used various procedures of sulfurization; one of them was also used in (18).

EXPERIMENTAL

Catalyst preparation. The supported catalysts used in this study (Pt/SiO_2, Cu/SiO_2, Pt/Al_2O_3, and Cu/Al_2O_3) were obtained by applying the wet impregnation method; the promoted catalysts ($PtSn/SiO_2$ and PtV/SiO_2) were prepared by coimpregnation. Proper amounts of both metal salts were dissolved separately in ethanol and then mixed together. Subsequently, the support material was added to the solution. After the solvent was evaporated under continuous stirring, the samples were dried in air for approximately 16 h at 383 K. Before testing, all catalysts were ground to powder and reduced *in situ* in a 15 ml min^{-1} (1 bar) hydrogen flow for 4 h—at 573 K for the platinum catalysts and at 483 K for the copper catalysts. Prior to the reduction step, all alumina-supported catalysts were calcined in a flow of oxygen at 520 K (20 $ml \cdot min^{-1}$) for 4 h. During this treatment strongly bound water and some chlorine species were removed. When copper is deposited on Aerosil at high pH, some copper ions stabilized by interaction with the support survive the standard reduction.

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The silica and alumina used as support materials were Aerosil 200 and γ-Al_2O_3 commercially available from Degussa and Ketjen, respectively. The precursors for the preparation of the catalysts were $H_2Pt(OH)_6$ (converted into H_2PtCl_6 by HCl) (Johnson Matthey Chemicals), $Cu(NO_3)_2 \cdot 3H_2O$, $SnCl_2 \cdot 2H_2O$ (>95%), and NH_4VO_3 (99.5%) (J. T. Baker).

The hydrogen (Hoek Loos 3.0, >99.90% purity) used was further purified by passage through a reduced copper deoxo catalyst (BTS) column and a column containing a molecular sieve. Acrolein (Merck, >99.5%) was distilled under nitrogen and dried for use with $MgSO_4$ (Brocacef, >99.5%).

Catalytic measurements. The catalytic experiments were performed in an all-glass flow apparatus. The flow apparatus was heated with heating wire to prevent condensation of the organic compounds on the inside of the glass tubes. In order to prevent polymerization of the (acid-, base- and) light-sensitive organic compounds all the glass tubes were protected against light by aluminum foil. The apparatus had to be cleaned regularly to ensure that no condensed and/or polymerized substances could disturb the results of the catalytic experiments.

The catalyst was situated on top of a glass grid, in a fixed-bed reactor with a diameter of about 15 mm. The heating and the temperature control of the reactor were achieved by a computer-regulated oven. The constant flow of hydrogen was purified by passing it over BTS to remove O_2 and then over a 4-Å molecular sieve to remove water. The gas flow rate was regulated by a calibrated mass flowmeter (Inacom Instruments b.v.). The catalysts were reduced *in situ* by passing the purified hydrogen (15 ml · min^{-1}) over the heated catalyst bed. After the reduction the reactor was cooled under hydrogen to the reaction temperature. For preparation of the planned reactions, the purified hydrogen was led through a saturator filled with (liquid) acrolein (at 248 K) and then through the reactor from top to bottom. Partial pressures of hydrogen and α,β-unsaturated aldehyde were 978 and 33 mbar, respectively. Samples of the reaction mixture were taken every 20 min with the help of an automatic sampling valve and were analyzed by a gas chromatograph (Chrompack 437A) equipped with a flame ionization detector (FID) and connected to an integrator (Spectra Physics SP4270). For product separation, the gas chromatograph was supplied with a 4 m × $\frac{1}{8}$ in. stainless steel column packed with 10% FFAP Chromosorb WHP (80/100 mesh).

The hydrogenations were performed either as a function of time-on-stream at a temperature or as a function of temperature with constant time-on-stream (60 min) at each temperature. In the latter experiments, the temperature was raised each hour by steps of 5 K. After the maximum temperature was reached, the temperature was decreased to the starting temperature in the same way. At each temperature three samples of the reaction mixture were analyzed by gas chromatography. Usually, the experiments were performed at low conversions to avoid secondary reactions as much as possible.

The stability in selectivities for all catalysts was very good, from O_3 to 16 h on stream (no measurements were performed for longer times). The activity (expressed here as *Yield* (8)) of unmodified platinum catalysts dropped within the first hour on stream but stayed constant thereafter. Sulfurized catalysts showed no sign of losing sulfur and no appreciable increase in activity with time-on-stream.

Irreversible modifications by sulfur. To test the effect of sulfur on the catalytic behavior of supported platinum and copper catalysts, three series of catalysts were presulfurized by using thiophene as the sulfur-donor molecule: (i) A *severe* (*ex situ*) presulfurization of the catalysts was accomplished by passing a flow (20 ml · min^{-1}) of a thiophene/H_2 (1/12) mixture over the freshly reduced catalyst at 570 K for 3 h. "Stripping" the catalyst, i.e., removing weakly bound sulfur and carbonaceous deposits, was done for 16 h at 670 K in a flow of hydrogen (20 ml min^{-1}). Furthermore, before the start of the catalytic experiment the presulfurized catalysts were rereduced at 720 K (*in situ*) by hydrogen (15 ml min^{-1}) for 5 h (20, 6). (ii) A *mild* (*in situ*) sulfurized catalyst was prepared by passing a 5 ml min^{-1} thiophene/H_2 (1/43) flow over the reduced catalyst at 298 K for half a minute, just before the start of the experiment. (iii) A mild sulfurization was also achieved by *injecting* 1 μl of liquid thiophene directly onto the freshly reduced catalyst (17, 18) at 353 K.

Acetylene pretreatment. After the apparatus was flushed with nitrogen for half an hour, the catalyst was pretreated with a 15 ml min^{-1} flow of N_2/acetylene (10/3) at 573 K for 1 h. Before the reaction was started, the continuous flow system was rinsed once more with nitrogen for half an hour. The reactions were performed at a constant temperature of 343 K.

Modifications of the surface by the reaction mixture itself. The aim of these experiments was to investigate the behavior of the Pt and PtSn (4 : 1 at%) catalysts during the very beginning of the reaction after various catalyst pretreatments. Therefore, 100-μl gaseous samples of the product mixture were taken after at least 3, 5, 8, 16, 32, 45, and 60 min with the help of two syringes. To prevent the acid-, base-, and light-sensitive product mixtures from polymerizing and condensing, the syringes were stored in a blinded oven (kept at 363 K) until the samples were analyzed:

1. A 5 wt% PtSn/Aerosil 200 catalyst was reduced at 573 K for 4 h. After 60 min the reaction was stopped and

the same sample was reduced again at 573 K for 16 h, prior to a second reaction. Both reactions were performed at a constant temperature of 350 K.

2. A 5 wt% PtSn/Aerosil 200 catalyst was calcined in oxygen at 773 K for 4 h and subsequently reduced at 458 K for 2 h. The reaction was carried out at a constant temperature of 350 K.

3. A 5 wt% Pt/Aerosil 200 catalyst was reduced at 473 K for 2 h prior to the reaction, which was performed at 348 K.

Transient CO modifications. CO pulses were recorded during the hydrogenation of acrolein over the 5 wt% PtSn/Aerosil 200 and the 5 wt% PtV/Aerosil 200 catalysts. The catalysts were reduced as usual in a 15 ml min^{-1} hydrogen flow at 573 K for 4 h prior to reaction. The hydrogenation reaction was performed at a constant temperature at 348 K. After the steady state was reached, the first CO pulse was injected into the feed at the entrance of the reactor with the help of a syringe. The catalyst was given approximately 1 h to recover from the CO pulse before introduction of the following one. The amounts of CO used in the hydrogenation reactions were: (i) 6x 5 μl in the case of the PtSn catalyst and (ii) 1x 50, 2x 40, and 2x 30 μl in the case of the PtV catalyst.

Experiments with various partial pressures. The influence of the acrolein/H_2 ratio on the selectivity and activity of the 5 wt% PtSn/Aerosil 200 catalyst was investigated. By variation of the temperature of the saturator (248, 258, and 262 K) hydrogenation reactions with respective acrolein/H_2 ratios of 1/30, 1/18, and 1/14 were achieved.

Data evaluation. To compare the results obtained with the catalysts in the various experiments the parameters selectivity and yield are used. The selectivity to a certain product i is defined as

$$S_i = \frac{n_i^P}{\sum_{i=1}^{k} n_i^P} \cdot 100\%.$$

Here, n^P is the number of moles of detected product i in the out stream after reaction. The activity of a catalyst in a specific reaction is characterized by the so-called yield of a product Y, which is a product of selectivity and activity, defined as

$$Y = \frac{S \cdot \alpha}{W},$$

with S as selectivity in %, α as the overall conversion of the reactant between 0 and 1, and W as the total weight of the catalyst in grams (8).

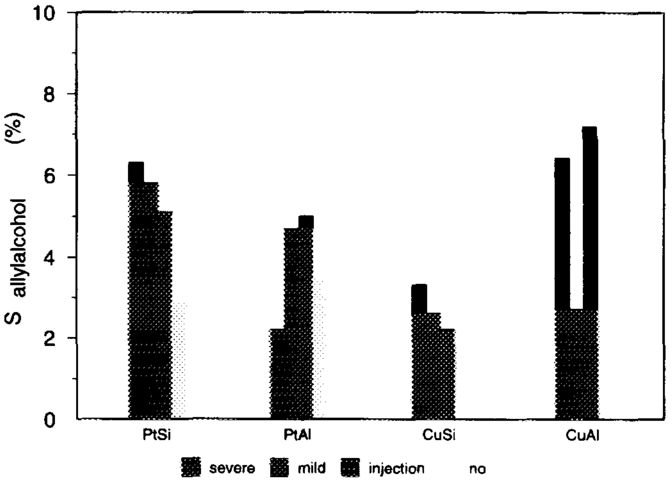


FIG. 1. Effect of different methods (bars, from the left to the right, represent severe, mild, and injection pretreatment) of sulfurization on the selectivity for allyl alcohol in the hydrogenation of acrolein over platinum- and copper-supported catalysts (supports, Si = SiO_2 and Al = Al_2O_3). Methods of sulfurization are described under Experimental. The well-reduced sulfur-free copper catalysts show a zero selectivity to allyl alcohol.

RESULTS

Modification of the catalysts by sulfur. In this study, two different supports—SiO_2 and γ-Al_2O_3—and two different metals—Pt and Cu—were used and the sulfurization was performed in three different ways (see Experimental), coded as "severe," "mild," and "injection."

Results concerning hydrogenation of acrolein under standard conditions are summarized in Fig. 1.

The pure platinum catalysts show a low but measurable selectivity to allyl alcohol, while the pure copper catalysts show virtually zero selectivity. After various sulfurizations of the copper catalysts a maximum selectivity of 8% was obtained; so the effect of sulfur on Cu is *relatively* large. However, none of the presulfurized catalysts reached as high a selectivity as reported in (19), i.e., a selectivity for allyl alcohol of 46%. It should be mentioned that catalysts containing Cu ions show a measurable selectivity for allyl alcohol.

Modification of the catalysts by carbonaceous layer deposition. The effect on activity and selectivity of carbon-rich, hydrogen-lean species deposited on the surface was investigated by adding acetylene led over well-reduced Pt and PtSn catalysts to the carrier gas before the reaction. In all cases, deactivation by reaction was suppressed and the yields dropped compared to the experiments without acetylene pretreatment.

An interesting difference between the Pt/SiO_2 and PtSn/SiO_2 catalysts has been observed. The same acetylene treatment suppresses the yields obtained with pure platinum catalysts by a factor of 4 to 5, but those obtained with PtSn/SiO_2 catalysts are suppressed by a factor of only 1.5 to 2. It is known that the presence of low(zero)-activity metal admixtures in a platinum catalyst suppresses hydrogenolysis (21, 22) of hydrocarbons, so that fewer deposits can be expected with PtSn catalyst than with pure Pt catalyst. The overall activity change is thus in agreement with this expectation.

Even more interesting than the activity suppression is the effect on the selectivity. Pure platinum has a very low selectivity for allyl alcohol; depending on the support used and the pretreatment of the catalyst applied, it varies between 0 and 5%. After pretreatment by acetylene this low selectivity of pure platinum disappears completely. However, the (macroscopically) same pretreatment of PtSn/SiO_2 catalyst does not change the selectivity for allyl alcohol, *S*.

In earlier papers (8) and in most of the literature (6, 7, 9–18) it was argued that with promoted catalysts the carbonyl group is activated to hydrogenation by the promoter (Sn ion or Sn metal atom). The active site can thus be described formally as Pt^0–$Sn^{\delta+}$ or Pt^0–Sn^0. Obviously, this site is not selectively poisoned by acetylene pretreatment.

Modification of the surface by the reaction mixture itself. The initial mixture (acrolein, H_2) used and the products of various reactions (alcohols, hydrocarbons C_xH_y, H_2O, CO) can modify the surface by oxidizing it, by segregating the catalyst compounds at the surface layer or by depositing inactive, carbonaceous species on the surface. The last effect has been described above. A closer look is now given to the effects of oxidizing reactions.

Figure 2 shows how the selectivity to different products develops during the initial stages of a reaction catalyzed by Pt/SiO_2. The formation of the alcohols is of minor significance here in comparison with that of propanal and propane. The selectivities for allyl alcohol and propanal increase in the first 16 min, while the selectivity for 1-propanol drops in the same period. The main feature to be kept in mind for later discussion is that the hydrogenolysis, i.e., formation of propane, is selectively suppressed by the initial self-poisoning. In this period of 15–20 min, the total conversion to detectable products decreases with increasing time-on-stream, from 50 to 5%. This initial self-poisoning during the first 20 min has the same consequences as the acetylene pretreatment.

As already mentioned, in relation to the acetylene pretreatment, admixture of Sn^0 with Pt^0 catalysts should lead to a suppression of hydrogenolysis. Such a change is observed, indeed (see Fig. 3). Figure 3 shows that with PtSn/SiO_2 relatively less propane is seen in the initial stages. The admixture of Sn and Pt catalysts evidently leads to a suppression of hydrogenolysis. When the PtSn catalyst is calcined before the reduction, propane is initially produced in rather large amounts (see Fig. 4). Since calcination in air leads to gas-induced segregation, the hydrogenolysis is now less suppressed by the presence of tin in the system than on well-reduced catalysts, with tin in the platinum surface. Furthermore, it can be seen in Fig. 3 that an *in situ* reduction of the PtSn catalyst suppresses the formation of allyl alcohol completely. However, the original selectivity can be restored after some time-on-stream.

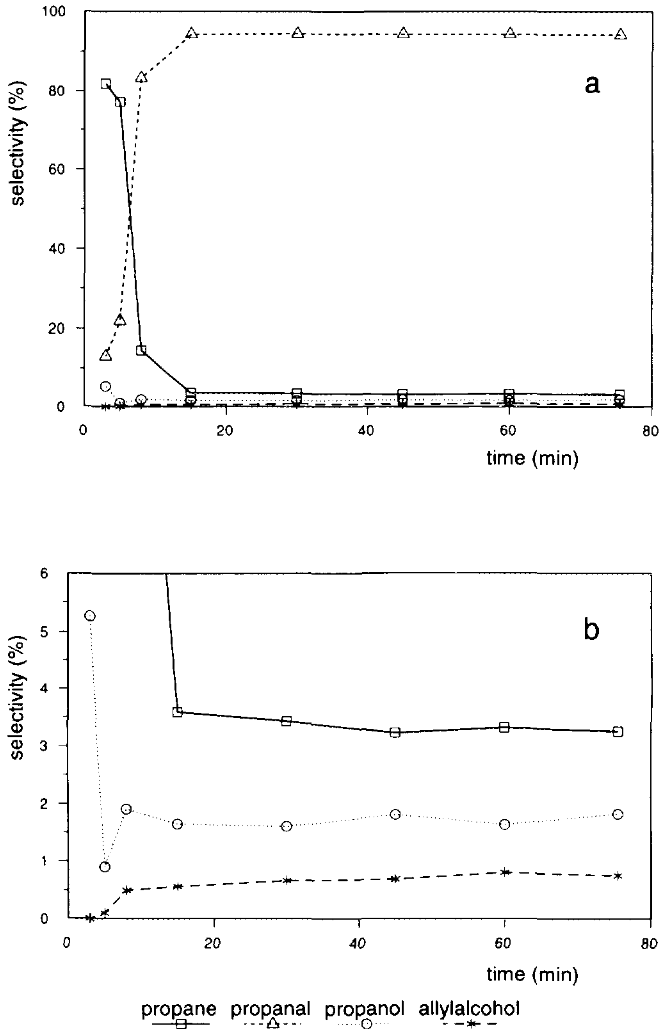


FIG. 2. (a) Development with time of the selectivities in acrolein hydrogenation over 5 wt% Pt/Aerosil 200. The catalyst was reduced at 473 K for 2 h prior to reaction, which was performed at a constant temperature of 348 K. (b) A blowup of the lower region of (a).

Modification of the selectivity by CO pulses. Carbon monoxide is known to displace adsorbed hydrogen (23) and adsorbed olefins (24) from the pure platinum surface. It can be expected that species containing a carbonyl group and interacting through it with a promoter on the Pt surface displace less readily than species bound

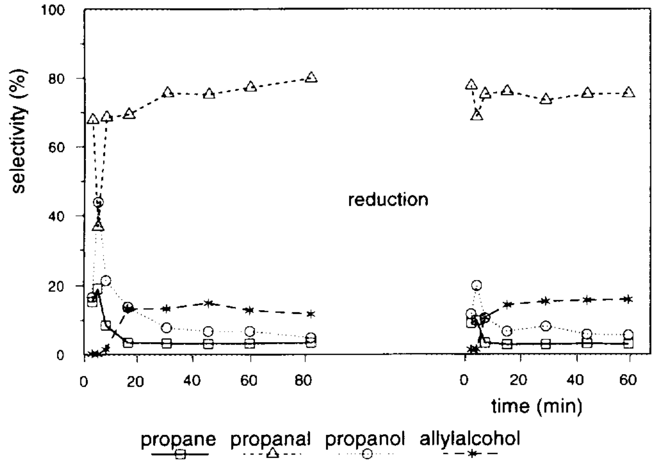


FIG. 3. Development with time of the selectivities in the hydrogenation of acrolein over 5 wt% PtSn/Aerosil 200. The catalyst was reduced at 573 K for 4 h; after 80 min the reaction was stopped and the sample was reduced at 573 K for 16 h prior to the second reaction. The temperature of both reactions was 350 K.

through the C=C bond (π-complexed species) or adsorbed hydrogen. With this knowledge in mind it was, therefore, interesting to investigate the effect of CO on the selectivity of the catalyst. Two catalysts were chosen for this test, $PtSn/SiO_2$ and PtV/SiO_2. Figure 5 shows a typical result for the selectivities obtained with the first-mentioned catalyst.

It should be mentioned that all yields decrease by the CO pulse. It can be seen from Fig. 5 that the selectivity to allyl alcohol is enhanced during the period of time in which carbon monoxide stays on the surface. When the pulse of CO is sufficiently high, *all* reactions are suppressed to zero, but also in this case poisoning is reversible.

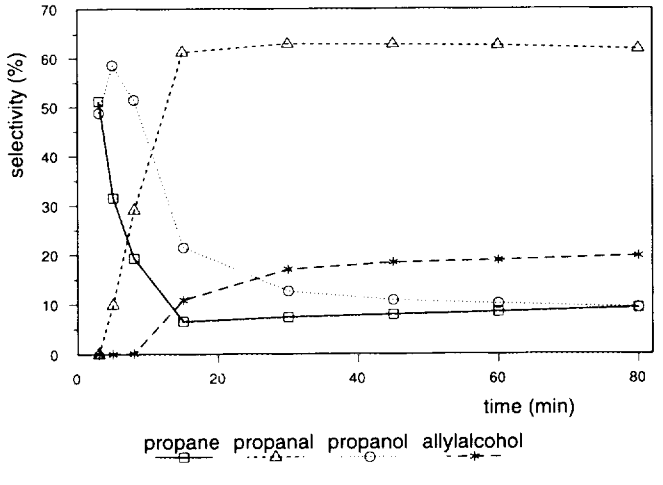


FIG. 4. Development with time of the selectivities in the hydrogenation of acrolein over 5 wt% PtSn/Aerosil 200. The catalyst was calcined at 773 K for 4 h and subsequently reduced at 458 K for 2 h prior to the reaction, which was performed at a constant temperature of 351 K.

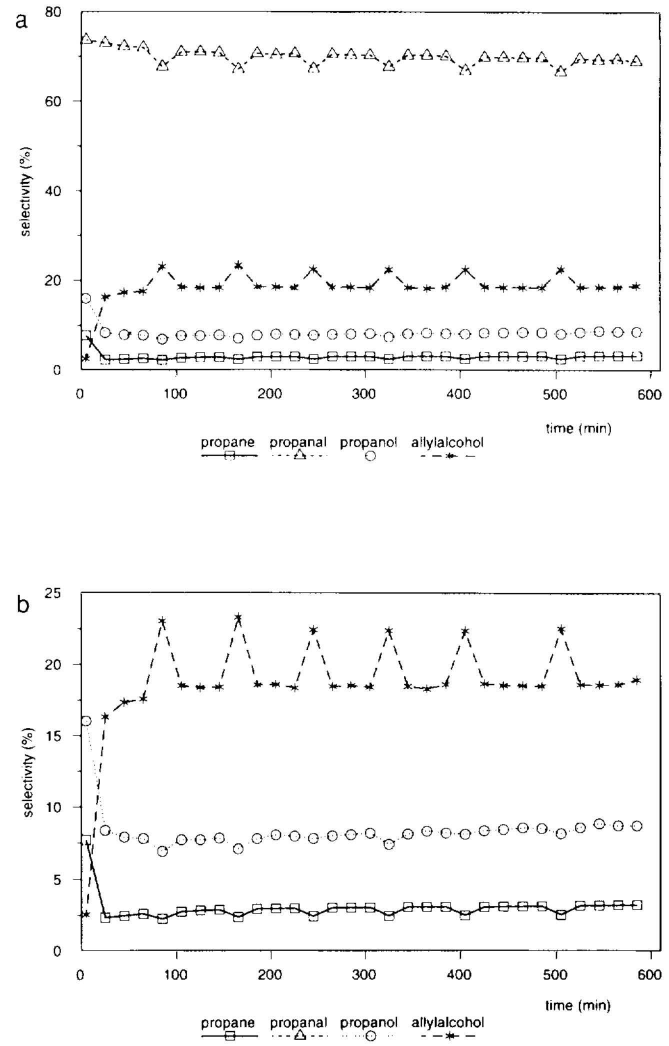
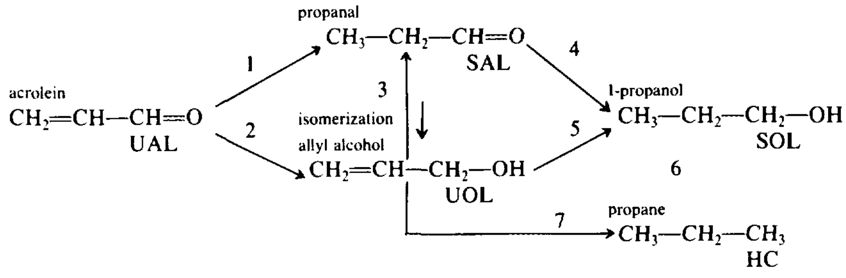


FIG. 5. (a) Product selectivities in the hydrogenation of acrolein over 5 wt% PtSn/Aerosil 200. Pulses of CO were injected repeatedly into the feed, 5 μl (6×). (b) A blowup of the lower region of (a).

DISCUSSION

Results presented above can be discussed on the basis of the reaction shown in Scheme 1. The occurrence of all reactions in Scheme 1 is well documented in the literature or was tested by monitoring the various reaction steps of separated components of the scheme (we have done it with steps 3, 4, 5, 6, and 7). Obviously, the most crucial step is the first splitting of the reaction, in steps 1 and 2.

The first influence on the selectivity of a PtSn catalyst to be considered is the effect of varying partial pressure, i.e., the ratio $p(H_2)/p(ACRO)$. According to the discussion below, a pronounced effect should not be expected



SCHEME 1

from changes in the partial pressures. If the selectivity is determined by the ratio of the reaction rates, then—with the likely rate determining steps—it can be defined, (using the symbols of Scheme 1):

$$S = \frac{r_{\mathrm{SAL}}}{r_{\mathrm{UOL}}} = \frac{N^{\mathrm{unprom}}}{N^{\mathrm{prom}}} * \frac{k_{\mathrm{SAL}}^{\mathrm{unprom}} * \Theta_{\mathrm{UAL}}^{\mathrm{unprom}} * \Theta_{\mathrm{H}}}{k_{\mathrm{UOL}}^{\mathrm{prom}} * \Theta_{\mathrm{UAL}}^{\mathrm{prom}} \cdot \Theta_{\mathrm{H}}}, \qquad [1]$$

where N stands for the respective numbers of sites, Θ for their coverages, and k for the rate constants. It is assumed here that propanal (SAL) is formed on unpromoted Pt^0 sites and allyl alcohol (UOL) in the Pt–Sn^{n+} promoted sites. On the condition that the adsorption is of the simplest Langmuirian type, and with a_i as adsorption coefficient, Eq. [1] gives Eq. [2] in the form

$$S = \frac{N^{\mathrm{unprom}}}{N^{\mathrm{prom}}} * \frac{k_{\mathrm{SAL}}^{\mathrm{unprom}}}{k_{\mathrm{UOL}}^{\mathrm{prom}}} * \frac{a_{\mathrm{UAL}}^{\mathrm{unprom}}}{a_{\mathrm{UAL}}^{\mathrm{prom}}} * \frac{p_{\mathrm{UAL}}}{p_{\mathrm{UAL}}}, \qquad [2]$$

and thus, approximately,

$$S \neq f(p_{\mathrm{H}_2}, p_{\mathrm{UAL}}).$$

This would make the ratio $r_{\mathrm{SAL}}/r_{\mathrm{UOL}}$, i.e., the selectivity, independent of the hydrogen pressure. This prediction agrees with our observation that changing of $p_{\mathrm{H}_2}/p_{\mathrm{UAL}}$ from 30 to 14 did not change the selectivity. Of course, it remains possible that the ratio S is influenced by side reactions, such as deposition of unreactive species, which *are* dependent on pressure.

The factor to be considered next is the possible role of the Pt ensemble size in selectivity. The average ensemble size can be varied easily by either dilution of Pt in an inactive (or much less active) metal or by poisoning of the surface with sulfur. The authors reported earlier (6) that neither of these manipulations enhanced the selectivity S_{UOL}. As mentioned in the Introduction, the absence of a positive effect of sulfur was surprising in view of the results presented by other authors (17–19). Therefore, additional experiments were performed to study the effect of various presulfurizations. Our newly obtained results (Fig. 1) confirmed the earlier results (6). To be able to compare results in (17) directly with ours, a series of presulfurized Cu catalysts was included in our study. The injection method was used in order to copy the preparation of the presulfurized catalysts as described in (17, 18). The standard temperature of the treatment with thiophene in (17, 18) differed from that in our study: they were 483 and 353 K, respectively. However, it was shown in (18) that if the Cu catalyst was treated at 353 K, the selectivity to the unsaturated alcohol was still higher than that with our catalysts. It is most remarkable that the three different methods of sulfurizing the alumina-supported Cu catalysts used in this study did not improve the selectivity either. There is no definitive explanation for the difference between the results in (17) and ours. However, considering the catalysts and pretreatments used in the mentioned paper, the following speculations can be formulated: If our hypothesis (see below) concerning the manner in which the promoters act to improve the selectivity is correct, the promotion effect is not achieved by a decrease in the size of the ensembles but by the presence of accessible and promoting cations (e.g., copper cations) on the surface of the metal. This would lead to the assumption that the authors of (17), by their preparation method or by their experimental conditions, formed unreducible Cu ions on the surface of Cu metal, whereas with our procedures that kind of distribution of cations (cations spread over the surface of Cu metal) did not occur.

The second possibility is that our thoughts about the unimportance of ensemble size are incorrect and that the authors of (17) achieved a better distribution of sulfur on the copper surface, leading to a better selectivity. If in our case sulfurization resulted—for whatever reason—in formation of compact islands of sulfide or sulfate species, no effect of decreasing ensemble size would be expected.

However, this suggestion is probably also incorrect, because we used the same molecule for sulfurization (thiophene) in our study as that used in (17). Furthermore, we used three different ways of sulfurization and one of these was a careful copy of the method used in (17).

The phenomena observed in the initial stages of the reaction are, in our opinion, helpful for a better understanding of the reactions studied. These phenomena can be analyzed with the help of Scheme 1. Important to this discussion is to acknowledge first what is already known about the state of pure Pt and $PtSn/SiO_2$ catalysts. Pure Pt catalysts, with SiO_2 as a support, probably contain only a very low concentration of unreduced Pt ions, while the Al_2O_3-supported platinum catalysts contain more Pt ions (25, 26). Both types of catalysts greatly expose the Pt metal (Pt^0) surface and show comparable, low selectivity for allyl alcohol (see Fig. 1).

$PtSn/SiO_2$ catalysts, when reduced at 573–673 K, contain Pt^0, Sn^0, and Pt–Sn alloy (intermetallic compounds) in addition to some Sn silicate. This is the conclusion of numerous papers reviewed recently (27, 28). The presence of Sn^0 in the metallic phase of the well-reduced catalyst seems to be guaranteed; the problem is whether the presence of SnO_x species on the working catalysts can be assumed as well. Very-well-reduced (673 K) catalysts (which because of their exposure to air certainly contained SnO_x) were compared with those reduced mildly (473 K), and the same selectivity was found. From other research concerning reactions of acetic acid/hydrogen mixtures on $PtSn/SiO_2$ catalysts, it is known (27–29) that (a) the catalysts containing SnO_x behave differently from the very-well-reduced $PtSn/SiO_2$ catalysts and (b) the mildly reduced $PtSn/SiO_2$ catalysts contain certainly SnO_x species (27, 28). This would mean that the very-well-reduced catalysts should be (quickly) covered by a certain amount of promoting SnO_x species during the initial stages of the reaction running on them. A close examination of the development of the acrolein hydrogenation over the Pt and PtSn catalysts during the first 20 min is now necessary to determine whether such modification of the $PtSn/SiO_2$ catalyst occurs.

The process of self-modification of the catalyst starts very quickly. The main changes observed in the induction period of the acrolein hydrogenation with pure Pt/SiO_2 catalysts (Fig. 2) are in propane and propanol production. Since the production of allyl alcohol is very low, we expect that the changes observed in the product distribution are a consequence of changes in the upper pathway in Scheme 1, i.e., changes on the line:

$$CH_2{=}CH{—}CH{=}O \xrightarrow{1} CH_3{—}CH_2{—}CH{=}O \xrightarrow{4} CH_3{—}CH_2{—}CH_2{—}OH \xrightarrow{6} CH_3{—}CH_2{—}CH_3 \quad [3]$$

In the initial stages of the reaction with the pure Pt catalyst there is a drop in total conversion and in particular a suppression of the hydrogenolysis to form propane. The occurrence of hydrogenolytic reactions requires large surface ensembles of Pt atoms (22). A suppression of these reactions indicates that the surface is covered by a protective inactive layer, such as a carbonaceous layer, polymeric species, or an oxidic or carbidic species (the exact nature is not known) during the first 15 to 20 min of the reaction. In contrast to hydrogenolysis, hydrogenations are known to be affected much less by blocking of active atoms on the surface (22). Thus, the formation of the products of steps 1 and 4 is still possible.

Results obtained with $PtSn/SiO_2$ presented in Fig. 3 can be explained in the same way. The formation of oxidic species in a catalyst with Sn is much easier and much more extended than that on pure Pt. Further, it should be considered that calcination leads to oxygen-induced segregation of Pt ensembles (PtO_x) on one side and SnO_x patches on the other side, which influences the course of the reaction. Namely, the hydrogenolysis is now less suppressed than that on well-reduced catalysts. In the case of the well-reduced catalysts, the SnO_x species are formed by the reaction itself and are better spread over the surface, which more efficiently diminishes the number of the Pt ensembles required for hydrogenolysis. Consequences of this phenomenon are shown in Fig. 4. Prereduction at only 458 K is obviously not sufficient to convert the SnO_x/PtO_x system back into Pt/Sn alloy (see Fig. 4). The presence of a proper promoter in the active form (e.g., SnO_x) makes the pathway via step 2 possible, which should lead to a higher formation of allyl alcohol. However, it was found that the hydrogenolysis of allyl alcohol to propane is very easy (easier than the hydrogenolysis of propanal (27)) and that there exists step 3 in scheme 1. As a consequence, this newly opened pathway via step 2 can also contribute to propane formation, on the condition that the state of the surface allows it. The right part of Fig. 3 shows that reduction at 573 K for 16 hours does not completely restore the clean unmodified surface either.

The results shown in Figs. 2–4 strongly support the idea that it is not the Sn^0 atoms (or $Sn^{\delta+}$ atoms) that are the promoting species but the SnO_x patches (Sn^{n+}), formed during the initial stages of reaction. Probably, these SnO_x patches are already present in the catalysts which were exposed to air and were not thoroughly reduced. This idea is also supported by the fact that dilution of Pt in the surface of well-reduced Pt–Cu catalysts (Cu is of relatively low activity) does not lead to an enhancement of selectivity for allyl alcohol. This information leads to the conclusion that the ensemble size effect does not influence the ratio of rates (see Eq. [1]). The main effect

FIG. 6. Adsorption of the olefinic group by "donation–back donation" (left) and by the adsorption of a carbonyl group by a donating "oxygen → metal" bond (right).

on the selectivity, as defined in Eq. [1], is due to the factors shown by Eq. [2].

Acrolein and all other α,β-unsaturated aldehydes must be adsorbed on centers of weak chemisorption so that they can enter steps 1 and 2 in Scheme 1. It is known that in hydrogenations of separated C=O and C=C groups the C=C is always hydrogenated faster and deeper (30). The latter is a thermodynamic effect, the former a kinetic effect. In simultaneous reactions involving both groups, the hydrogenation on C=C is again the easier one. It appears that this is because of the weak adsorption through the C=O group (31). An obvious conclusion is that this adsorption must be strengthened. Taking into account the results of IR and EELS concerning adsorption of aldehydes and ketones (32), as well as the theoretical analysis of chemisorption bonds [33], we can conclude that the "dative" adsorption of C=O (see Fig. 6, right side) is weaker than the π-complexing of the C=C bond (see Fig. 6, left side). However, adsorption as in Fig. 6 (right) can be strengthened when * bears a positive charge, as it does in promoting SnO_x.

Carbon monoxide displaces most of the adsorbed species from the surface, but one can conclude that consistent with the picture of promoter effects as just described, it disturbs hydrogenation of the aldehyde bound to the Pt–Sn^{n+} site less than hydrogenations on the pure platinum surface.

CONCLUSIONS

Selectivity in the hydrogenation of the α,β-unsaturated aldehydes is influenced mainly by the presence of sites on the catalysts, which activate the aldehydic oxygen and permit an easy supply of hydrogen atoms. The effect of the ensemble size is much less important. Sulfurization (when oxidation of copper is prevented) causes only a marginal effect on selectivity. Small selectivity effects can be also caused by gas modifiers like carbon monoxide.

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