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Activity and Selectivity in the Reactions of Substituted α,β-Unsaturated Aldehydes

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The effect of substitution of α,β-unsaturated aldehydes on the activity and selectivity of a series of platinum catalysts was investigated for the hydrogenation of these compounds. The silica-supported platinum catalysts were promoted by a selected group of additives: compounds of Na (alkali metal), V, Ti, Fe (transition metals), Ga, Sn, and Ge (nontransition elements). For all catalysts the selectivity to unsaturated alcohol (UOL) increased with increasing substitution on the terminal olefinic carbon atom (crotonaldehyde and methyl-crotonaldehyde, respectively). This indicates that the adsorption modes are related to selectivity and the selectivity is influenced by the competition of the C=O and C=C group for the same sites on the promoter. In the hydrogenation of methacrolein, wherein the methyl substituent is located on the internal olefinic carbon atom, and in the hydrogenation of methyl vinyl ketone, very pronounced differences in the selectivity to UOL were observed. The trends in activity and selectivity indicate that the substitutional effects are mainly steric in origin. In general, the activity of a specific group decreases with substitution on that group.

INTRODUCTION

Screening of the literature on that subject reveals (1–9) that the title reactions are of considerable practical and fundamental interest. The hydrogenation of α,β-unsaturated aldehydes (UAL) can result in the formation of the corresponding hydrocarbon (HC), saturated aldehyde (SAL), unsaturated alcohol (UOL), and saturated alcohol (SOL). In attempts to achieve an as high as possible selectivity to the desired unsaturated alcohols the following problems are encountered: (i) From the point of view of thermodynamics it is always more profitable to produce a saturated aldehyde or saturated alcohol than the unsaturated alcohol. Obviously, nothing can be changed in that (thermodynamic) respect simply by using different pure metals as catalyst. (ii) It is known (10) that the reactivity of the unsubstituted isolated C=C group in hydrogenations with unpromoted metals is always higher than the reactivity of the isolated aldehydic or ketonic group. To change this situation will be not easy, but there is some chance of success by manipulating the properties of certain catalysts. As already mentioned under (i), variation of the metal component will result in small improvements only. Except for Pd, which is very inactive with regard to the C=O group, other metals form very similar sequences in activities (10) for separately running hydrogenations of the C=O and C=C bonds. Thus, it can be expected that the choice of metal influences the activity more than the selectivity. However, it should be possible and, as reported in literature it is possible indeed (see, e.g., Refs. (1), (11), and (12)) to enhance the reactivity of the C=O group without changing that of the C=C group. In our first paper concerning this problem, the manipulations of the selectivity by using various promoters are described (13). As a result of that first study the promoters were divided in the three groups:

I. alkali metal ionic compounds,

II. transition metal compounds,

III. nontransition element (Sn, Ge, Ga) compound, with an increase of the promoting effect in the order I < II < III. Our findings with acrolein, which confirmed already published information concerning similar hydrogenations, did raise the question why promoters which activate so well the isolated C=O groups (4), or the CO molecule (14) are apparently inferior in activating the C=O groups of α,β-unsaturated aldehydes? A working hypothesis was formulated based on the assumption that the metal ions of the transition-metal oxides can bind not only the C=O group, but also the C=C group. According to this hypothesis it could be expected that the *relative* accessibility and the binding strength to the catalyst of the C=C and C=O groups in various α,β-unsaturated aldehydes is important for the selectivity. To prove the validity of this idea, two series of molecules substituted at either the C=C or at the C=O group were selected and their selectivity in the hydrogenation to unsaturated alcohols were compared. If, with a given promoter the selectivity to UOL really depends on binding of the C=C group to the promoter, a steric hindrance created on this group should change the selectivty.

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EXPERIMENTAL

Materials. The platinum catalysts were supported on a very pure inert silica, Aerosil 200 (Degussa, 200 m^2/g). The precursors used for the preparation of the (un)promoted platinum catalysts were $H_2Pt(OH)_6$ (Johnson Matthey Chemicals), which is converted into H_2PtCl_6 by HCl, and $SnCl_22H_2O$ (>95%), NH_4VO_3 (99.5%) (J. T. Baker), $GeCl_4$ (99.99%), $Fe(NO_3)_39H_2O$ (99%) (Janssen Chimica), $Ti(OC_2H_5)_4$ (Johnson Matthey Chemicals), $GaCl_3$, NaCl (>99.5%) (Merck).

Hydrogen (Hoekloos >99.90% purity) which was used was further purified by passage through a column filled with BTS and molecular sieve. Acrolein (Merck, ~95%), crotonaldehyde (Aldrich, 99+%), 3-methyl-crotonaldehyde (Merck, >96%), methacrolein (Aldrich, 95%), and methyl vinyl ketone (Fluka, ≥99%) were distilled under nitrogen before use.

Catalyst preparation. The catalysts were obtained by applying the wet impregnation method. The metal loading of the platinum catalysts was 5.0 wt%, and the compound of the promoting element X was coimpregnated in a molar ratio of $Pt : X = 4 : 1$. First, proper amounts of both metal salts were dissolved separately in ethanol or water and then mixed. Subsequently, the support was added to the solution. After evaporating the solvent under nitrogen atmosphere and continuous stirring, the samples were dried over night at 383 K in air.

Catalyst characterization. The formation of alloys and the particle sizes of the freshly reduced catalyzed were determined by XRD. The XRD measurements (usually scanned in the range $10° < 2\Theta < 70°$) were performed on a Philips Goniometer PW1050/25 equipped with a PW Cu 2103/00 X-ray tube. Additional information on the homogeneity in the particle size and the particle size distribution was obtained by TEM for the platinum catalysts promoted by vanadium, gallium, germanium, and tin. The TEM data were collected with a Philips EM420. which operated at 120 kV. A rough estimate of the promoter free metal surface has been made by measuring the CO adsorption from a flow of carrier gas, using the Quantasorb adsorption apparatus (Quantachrome).

Apparatus and procedure. The catalytic experiments were performed in an all-gas 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 make sure no condensed and/or polymerized substances were disturbing 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. A constant flow of hydrogen was purified by passing it over a reduced copper deoxo catalyst (BTS) (to remove O_2) and a 4 Å molecular sieve (to remove water), respectively. The gas-flow rate was regulated by a conventional mass flow controller. Prior to the experiments the catalysts were reduced *in situ* by passing the purified hydrogen (15 $ml \cdot min^{-1}$) over the heated catalyst bed. The reduction temperature for the platinum catalysts was 573 K. After the reduction the reactor was cooled down to the reaction temperature under hydrogen. In order to perform the reaction the purified hydrogen was led through a saturator, filled with the organic reactant under study, and subsequently, from top to bottom, through the reactor. By adjusting the temperature of the saturator the desired ratio of hydrogen and the organic reactant could be obtained. In standard experiments, partial pressures of hydrogen and the α,β-unsaturated aldehyde were 978 and 33 mbar, respectively. The flow rate of reactant in the standard experiments was 2.09×10^{17} $molecules/s^{-1}$. When the ratio of P_{H2}/P_{UAL} is changed from about 30 (standard experiment) to about 14, no change in selectivity is observed.

The hydrogenations were performed as a function of temperature, with a prefixed time on stream (60 min) at each temperature. In these experiments the temperature was raised each hour by steps of 5 K. After reaching the maximum required temperature, the temperature is brought down to the starting temperature in the same way. In 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. Samples of the reaction mixture were taken with the help of an automatic sampling valve and analyzed by gas chromatography.

The gas chromatograph used was a Chrompack 437A, equipped with a flame ionization detector (FID). The gas chromatograph was equipped with a 4 m × ⅛ in. stainless-steel column packed with 10% FFAP Chromosorb WHP (80/100 mesh). The temperature of the column was adjusted to achieve the optimal separation of the organic reactant under study and its reaction products. The data collection and evaluation was accomplished by coupling the gas chromatograph to a Spectra Physics SP 4270 integrator. The heating and the temperature control were achieved by a computer regulated oven.

Data evaluation. The results obtained with the catalysts in the various experiments were interpreted in terms of the selectivity and yield. 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 product i in the flow after reaction. The activity of a catalyst in a specific reaction is characterized by the so-called yield of product Y, which is a combination of selectivity and activity, defined as

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

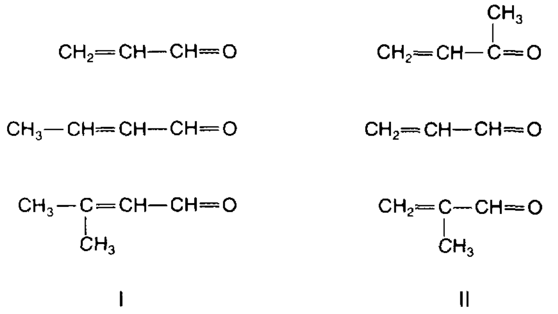
with S as selectivity in %, α as the overall conversion of the reactant between 0 and 1, and W as the total weight of the catalyst in grams.

RESULTS

The XRD and TEM results showed that with all promoted catalysts the addition of the promoter did not significantly alter the particle size. For example, the particle size calculated from line broadening was in the Pt/SiO_2 catalyst 10.5 nm, and in promoted PtX/SiO_2 catalysts between 8.5 and 15 nm. PtV, PtGa, and PtGe also showed in electron micrographs a fraction of small particles (2–3 nm). Pt–Sn was the only system which showed small amounts of alloys formed upon reduction. This system showed a remarkable homogeneity in the particle size distribution. Carbon monoxide adsorption measurements revealed that in all cases (except with alkali additives) promoters occupied a large part of the metal surface.

A few words about the most likely state of the promoters are in order. Reduction temperature is rather low to expect reduction to metal of V, Ga, and Ge compounds. In compliance with that, no alloy formation is observed. Some alloying was observed with Pt–Sn. Therefore, in a separate experiment, the the Pt–Sn-reduced catalyst was oxidized at 673 K in air (clearly, the platinum and tin-containing phases separate) and then reduced only at 473 K. This catalyst showed the same selectivity as that reduced at 573 K. Further, a parallel research on acetic acid reduction (15) revealed that Pt–Sn alloys and $Pt\text{–}SnO_{2-x}$ catalysts behave very differently. The catalysts as used in our standard experiments behaved in acetic acid reduction as $Pt\text{–}SnO_{2-x}$. Therefore, we consider it justified to assume that the promoter is active by its cations, which either survive the reduction or are formed by the first contact with aldehydes.

In an earlier study (13) the activity and selectivity values that had been obtained in the hydrogenation of acrolein over platinum catalysts promoted by a large variety of additives were presented. Here, a selected group of promoters was used in the hydrogenation experiments with two series of methyl-substituted aliphatic α,β-unsaturated aldehydes shown in Fig. 1.



$CH_2{=}CH{-}CH{=}O$ $\quad$ $CH_2{=}CH{-}C(CH_3){=}O$

$CH_3{-}CH{=}CH{-}CH{=}O$ $\quad$ $CH_2{=}CH{-}CH{=}O$

$CH_3{-}C(CH_3){=}CH{-}CH{=}O$ $\quad$ $CH_2{=}C(CH_3){-}CH{=}O$

I $\quad$ II

FIG. 1. The two series of α,β-unsaturated aldehydes studied: I, acrolein, crotonaldehyde, 3-methyl-crotonaldehyde; and II, methyl vinyl ketone, acrolein, methacrolein.

In series I, the $R_1R_2C{=}CH{-}CH{=}O$ molecules, the basic skeleton is substituted on the terminal olefinic carbon atom with either one ($R_1{=}CH_3$, $R_2{=}H$ in crotonaldehyde) or two ($R_1{=}R_2{=}CH_3$ in 3-methyl-crotonaldehyde) methyl groups. In order to compare the effect of a methyl substituent on the olefinic group with one on the carbonyl group, the $CH_2{=}CR_3{-}CR_4{=}O$ molecules were studied. The skeleton in series II was substituted either on the internal olefinic carbon atom ($R_3{=}CH_3$, $R_4{=}H$ in methacrolein) or on the carbonylic carbon atom ($R_3{=}H$, $R_4{=}CH_3$ in methyl vinyl ketone).

As mentioned above, only a small selection of promoters was used here, representative of the different groups of elements: Na (alkali metal), V, Ti, Fe (transition metals), Ga, Sn, and Ge (nontransition elements). The reaction conditions and the molar ratio of hydrogen and organic reactant were kept constant.

The activity and selectivity values were determined at 353 K in the decreasing range of the temperature program. This temperature and the way of comparison was chosen after a more detailed study performed with the $PtSn/SiO_2$ catalyst. In one of the experiments, the temperature range in which the catalytic measurement has been done was scanned three times. The main activity decrease takes place during the first run (a run with increasing temperature) and a pseudo-steady state of the catalyst is then achieved.

It is important for this study that the selectivities as discussed below are only marginally changing with temperature or with deactivation of the catalysts. These changes are much smaller than the differences discussed.

Figure 2 shows that the selectivity to unsaturated alcohol increased for all promoted- and unpromoted-platinum catalysts with increasing substitution on the terminal olefinic carbon atom.

Special attention should be paid to the changes in selectivity in the case of the iron-promoted catalyst. Iron salts have proved to be good promoters in the hydrogenation of carbon monoxide (16) and of an isolated carbonyl group (e.g., acetone, Ref. (4)). The ability of the iron cations to activate the olefinic group as well or even better than the carbonylic group might be responsible for the "unexpect-

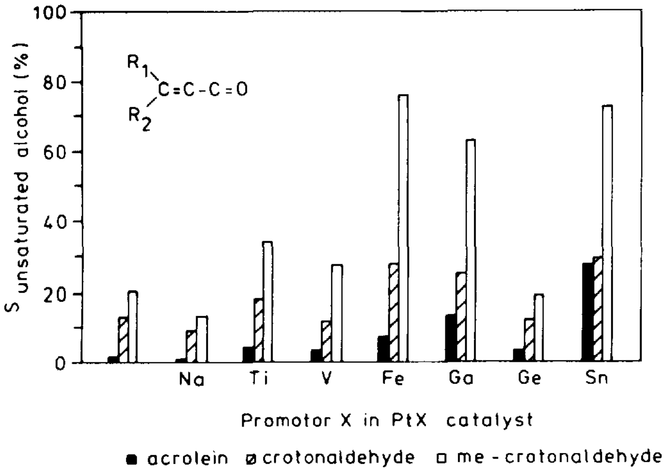


FIG. 2. Selectivity to unsaturated alcohol in the hydrogenation of acrolein, crotonaldehyde, and 3-methyl-crotonaldehyde over promoted platinum catalysts.

edly" low selectivity to the unsaturated alcohol in the hydrogenation of an unsubstituted α,β-unsaturated aldehyde like acrolein. To test this idea was one of the main aims of the investigations described here. As shown by experiments with reactants of series I (see Fig. 1), iron promoters increase the activity (Table 1a,b,c) and the *selectivity* (Fig. 2) in the formation of unsaturated alcohol, on condition that the olefinic group is sterically hindered by methyl substituents. This result seems to comfirm the working hypothesis very clearly.

In series II, a comparison of methacrolein with acrolein reveals (Fig. 3) that the selectivity to unsaturated alcohols with these two molecules is approximately the same with some catalysts. However, an increase of the desired selectivity by a factor of 2 is observed with the titanium- and vanadium-promoted catalysts and even by a factor of 6 with the germanium-promoted catalyst. The selectivity to saturated aldehyde (Table 2a,b) is higher in the hydrogenation of acrolein than of methacrolein.

In the hydrogenation of methyl vinyl ketone a dramatic drop in the selectivity to unsaturated alcohol compared to acrolein was observed. Obviously, the presence of a methyl group (R_4) on the carbonylic carbon atom made the adsorption and activation of the ketonic group almost impossible. These results corresponded with earlier measurements of others (17), who were also unable to produce unsaturated alcohols from unsaturated ketones.

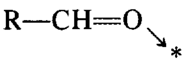
Surprisingly high is the activity for the formation of saturated aldehyde (Table 2c) in the hydrogenation of methyl vinyl ketone. In contrast to the hydrogenation of the α,β-unsaturated aldehydes, where the deactivation in the first hour is considerable, the deactivation in the course of the experiment with methyl vinyl ketone is negligible (see Fig. 4). According to these observations it seems that in the hydrogenation of methyl vinyl ketone no essential carbonaceous or polymeric deposits are formed on the catalyst. Although the yield for the saturated alcohol is also quite high, the very high yield of the saturated aldehyde is the result of the primary selectivity to the saturated aldehyde (Table 2c).

DISCUSSION

Our earlier paper (13) brought the evidence that a subdivision of the metal surface in smaller ensembles by inactive copper or sulphur atoms does not lead to any appreciable increase in selectivity. It cannot be reasonably expected that a zero-valent tin would behave differently from copper. On the other hand we have strong indications that in all cases ionic species of the promoter are present and therefore we assume their promoting effects in the discussion which follows. This raises the question of where these promoting species are located. Promoters alone (platinum free) are inactive. We assume that the promoter on SiO_2 far from a metal particle is inactive, too. In an additional experiment the Aerosil surface was covered by tin oxide and platinum mounted on it from a solution which did not dissolve tin oxide. This catalyst which had tin oxide only under the metal particles showed the same selectivity as pure, promoter-free platinum. Similar experiments have been done earlier with the syngas reaction and there it appeared that promoter can exert its activity only when it is on the metal; being only under the metal, it is without any effect (18). Since with all catalysts (except the alkali promoted) studied in this paper a large part of the metallic surface is covered by promoting components, we assume below that promoters act being *on* the metal.

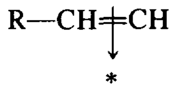
Chemisorption of aldehydes and ketones on one side and chemisorption of olefines on the other side shows both very similar adsorption modes, as revealed by studies with various vibration spectroscopies. Below, only a few references are mentioned, just for illustration:

1. Adsorption by "donation–back donation" mechanism. In most cases the donation is more important and with aldehydes it is perhaps even the exclusive mechanism (19).



$$R{-}CH{=}O \searrow *$$

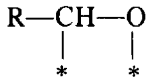
a



$$R{-}CH{\overset{}{=}}CH \ \downarrow \ *$$

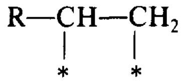
b

2. Di-σ-bond formation (20–22):



$$\begin{array}{ccc} R{-}CH & {-} & O \\ | & & | \\ * & & * \end{array}$$

c



$$\begin{array}{ccc} R{-}CH & {-} & CH_2 \\ | & & | \\ * & & * \end{array}$$

d

TABLE 1

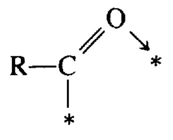
Activity and Selectivity in the Hydrogenation of Acrolein, Crotonaldehyde, and 3-Methyl-Crotonaldehyde over Promoted Pt/Aerosil 200 Catalysts

Catalyst	Yield				Selectivity (%)			
	Y_{HC}	Y_{SAL}	Y_{UOL}	Y_{SOL}	S_{HC}	S_{SAL}	S_{UOL}	S_{SOL}
a. Hydrogenation of acrolein (CH_2=CH-CH=O)								
Pt	16	372	7	7	4.0	92.6	1.6	1.8
PtNa	21	2009	18	24	1.0	96.9	0.9	1.2
PtTi	6	160	8	5	3.3	89.7	4.2	2.8
PtV	25	642	24	22	3.5	90.0	3.4	3.1
PtFe	10	1854	158	161	0.4	84.9	7.3	7.4
PtGa	7	185	33	20	2.8	75.6	13.2	8.4
PtGe	7	146	5	3	4.5	90.7	3.2	1.6
PtSn	7	191	79	8	2.6	67.0	27.5	2.9
b. Hydrogenation of crotonaldehyde (CH_3-CH=CH-CH=O)								
Pt	6	89	23	60	3.4	50.0	13.0	33.6
PtNa	8	185	27	77	2.6	62.5	9.0	25.9
PtTi	8	119	48	89	3.2	45.0	18.2	33.6
PtV	46	862	147	223	3.6	67.4	11.5	17.4
PtFe	34	1329	825	774	1.2	44.9	27.8	26.1
PtGa	32	1204	752	1002	1.1	40.3	25.1	33.5
PtGe	8	142	34	105	2.7	49.1	11.9	36.4
PtSn	16	828	488	321	1.0	50.1	29.5	19.4
c. Hydrogenation of 3-methyl-crotonaldehyde (CH_3-C(CH_3)=CH-CH=O)								
Pt	42	96	116	311	7.5	17.0	20.5	55.0
PtNa	6	208	76	273	1.1	36.9	13.4	48.6
PtTi	16	97	230	138	3.0	18.8	33.7	44.5
PtV	12	92	130	241	2.5	19.5	27.4	50.6
PtFe	3	112	1758	315	0.1	5.1	80.4	14.4
PtGa	5	44	699	292	0.5	4.3	67.1	28.1
PtGe	38	124	115	315	6.6	20.9	19.4	53.1
PtSn	0	277	2834	543	0.0	7.6	77.5	14.9

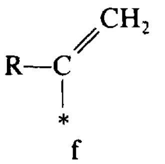
Note. The rate of reaction, $r_i = Y_i \times 2.09 \times 10^{15}$ in units of molecules/(g cat. s).

Note: It must be mentioned here that on Pd mode "b" is more abundant than mode "d," while on Pt it is vice versa (19).

3. Dissociatively adsorbed species (23–24), for example



e



f

With respect to the forming of molecular orbitals, the similarity between the complexes on the left- and right-hand side is easily recognizable. This is the principle reason why it is so difficult to succeed in improving only the left or the right part of the above-described modes, for instance, by replacing one metal with another.

The only chance to influence the selectivity is to introduce promoters that can activate the C=O group without binding (adsorbing) the C=C group. Transition metal oxides (i.e., their cations) can form both complexes a and b, which means that improvement of the selectivity to the unsaturated alcohol could be limited by that. On the other hand, the nontransition metal cations would likely activate the "a" mode much more than the "b" mode (if mode b exists at all, in this context).

A very likely adsorption mode expected to be present and active in the oxygenate formation from synthesis gas (14) is essentially complex "e". Its counterpart, "f", is according to vibrational spectroscopy results [23, 24] not very active. It is not clear exactly what makes promoters of groups II (transition metal compounds) and III (nontransition element compounds) to behave so differently, if the two adsorption modes e and f were the only intermediates of hydrogenation stimulated by promoters. There-

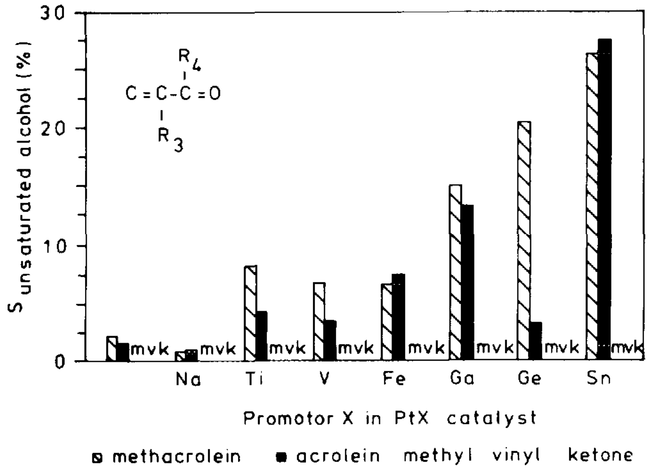


FIG. 3. Selectivity to unsaturated alcohol in the hydrogenation of methacrolein, acrolein, and methyl vinyl ketone over platinum catalysts.

fore, other intermediates should also be considered and species a–e compared. The following question is raised: Do the substitution effects observed with series I and II of the reactants (see Fig. 1) confirm the assumption that with the transition metal oxide promoters, adsorption through the olefinic bond (modes b and d) hinders or even prevents all the adsorption modes which activate the oxygen end of the aldehyde (modes a, c, and e)?

To answer that question, the effects of substitution on the olefinic bond must be evaluated more carefully. It then turns out that whatever substitution is present on the olefinic bond, the *reactivity* of this group is always decreased (see Table 1). Even without any detailed knowledge about the quantitative aspect of this decrease in reactivity, qualitatively the result is favorable because of the enhanced selectivity to unsaturated alcohol. As known from literature (Refs. (1) and (7)) the substitution by a phenyl group on the olefinic group (i.e., cinnamaldehyde) also leads to an increase in the selectivity to unsaturated alcohol, and the selectivity is always higher than that observed with acrolein.

Substitution on the $C=O$ group also has a retarding effect which, however, is much more pronounced than that achieved by substitution on the olefinic bond, as can be seen in Fig. 3. This very dramatic effect makes *complex e* a very attractive candidate to be used as one of the intermediates to explain the selective activation of the $C=O$ group. Because of the absence of a hydrogen atom on the $C=O$ group in the ketonic compounds, a dissociative adsorption with mode e is impossible. Thus, adsorption modes a and b would be the only remaining possibilities for ketone hydrogenation. The adsorption mode of the carbonylic group (mode a) is a weak one and is therefore always easily displaced by the stronger adsorption of the olefinic group (mode b). This is, in our opinion, the reason for the high yield of the saturated aldehyde as the main product in the hydrogenation of methyl vinyl ketone (see Table 2c).

Finally, it is worthwhile considering the origin of the substitution effects described above. The substitution by one or more methyl groups onto the olefinic and the carbonylic groups obviously has a distinct influence on the activity and selectivity. According to literature concerning the electronic effects of substitution (25, 26), activity effects in the hydrogenation of isolated groups in molecules with varying (Hammett, Taft-) σ-coefficients are practically the same for substitution on $C=O$ and $C=C$ groups (see the graphs in Refs. (25) and (26)). This means that the substitution of an H atom by a CH_3 group should have a similar effect on the hydrogenation of the $C=C$ and on the $C=O$ group. However, the hydrogenations of methacrolein and methyl vinyl ketone (see Tables 2a and 2c) show an observable but modest effect on the $C=C$ hydrogenation, in contrast with the most dramatic effect on the hydrogenation of the $C=O$ group (compare methyl vinyl ketone with acrolein in Table 2b). From these observations we conclude that substitution effects are mainly *steric* in origin.

Further we conclude that results obtained with substituted molecules confirm that the selectivity is related to the competition of the $C=O$ and $C=C$ groups for the same site on the promoter.

The data presented in Tables 1 and 2 do not allow a fully quantitative discussion on the activity; nevertheless, it seems useful here to place several remarks. The yields expressed as rates per unit surface area show that various promoters influence the activity to different degrees. This is not surprising since, in our opinion, a promoter has mainly the following three effects: (1) It activates the $C=O$ group for hydrogenation. (2) It can prevent the deposition of polymeric fragments on the surface. As a consequence, promotion can cause an increase in the rate of reaction. (3) The activity effects of a promoter should show a maximum when its concentration on the surface is varied. At high contents of promoter, the rate should be low again due to the blocking effect of promoter species.

Without an exact knowledge of the metal surface coverage by the promoter and without determination of polymeric layers on the metal obviously no quantitative conclusion can be drawn. Qualitatively, the data suggest that methyl vinyl ketone is unable to form polymeric deposits.

With respect to the rates of hydrogenation of crotonaldehyde and methacrolein a systematic difference is observed (see Tables 1b and 2a, respectively). These two molecules have the same number of carbon atoms and they differ only by the position of the CH_3 substituent.

CONCLUSIONS

It was proposed in the earlier study (13) concerning the selective hydrogenation of acrolein over modified plati-

TABLE 2

Activity and Selectivity in the Hydrogenation of Methacrolein, Acrolein, and Methyl Vinyl Ketone over Promoted Pt\Aerosil 200 Catalysts

	Yield				Selectivity (%)			
Catalyst	Y_{HC}	Y_{SAL}	Y_{UOL}	Y_{SOL}	S_{HC}	S_{SAL}	S_{UOL}	S_{SOL}
a. Hydrogenation of methacrolein ($CH_2{=}C(CH_3){-}CH{=}O$)								
Pt	2	31	1	1	6.4	88.3	2.2	3.0
PtNa	4	252	2	3	1.7	96.2	0.8	1.3
PtTi	3	66	6	4	3.7	83.3	8.2	4.8
PtV	3	86	7	6	3.3	83.8	6.7	6.2
PtFe	3	231	19	39	1.1	79.0	6.6	13.4
PtGa	3	116	24	21	1.8	70.3	14.9	12.9
PtGe	2	56	17	8	2.6	67.5	20.4	9.6
PtSn	3	164	70	31	0.9	61.3	26.3	11.4
b. Hydrogenation of acrolein ($CH_2{=}CH{-}CH{=}O$)								
Pt	16	372	7	7	4.0	92.6	1.6	1.8
PtNa	21	2009	18	24	1.0	96.9	0.9	1.2
PtTi	6	160	8	5	3.3	89.7	4.2	2.8
PtV	25	642	24	22	3.5	90.0	3.4	3.1
PtFe	10	1854	158	161	0.4	84.9	7.3	7.4
PtGa	7	185	33	20	2.8	75.6	13.2	8.4
PtGe	7	146	5	3	4.5	90.7	3.2	1.6
PtSn	7	191	79	8	2.6	67.0	27.5	2.9
c. Hydrogenation of methyl vinyl ketone ($CH_2{=}CH{-}C(CH_3){=}O$)								
Pt	9	16107	23	527	0.1	96.6	0.1	3.2
PtNa	23	17983	0	2401	0.1	88.1	0.0	11.8
PtTi	0	19293	33	1082	0.0	94.5	0.2	5.3
PtV	28	18533	0	1847	0.1	90.8	0.0	9.1
PtFe	17	17101	39	3293	0.1	83.8	0.2	15.9
PtGa	79	18389	46	1639	0.4	91.3	0.2	8.1
PtGe	24	19311	48	962	0.1	94.9	0.3	4.7
PtSn	32	21412	14	794	0.1	96.2	0.1	3.6

Note. The rate of reaction, $r_i = Y_i \times 2.09 \times 10^{15}$ in units of molecules/(g cat. s).

num catalysts that the competitive adsorption of the olefinic and the carbonylic group plays an essential role. An idea was expressed that the difference in the reactivity should be related to the adsorption modes of the olefinic bond on the one side and of the aldehydic (ketonic) bond on the other side. This study shows clearly that substitution on the olefinic group expresses the adsorption through this group: the more methyl groups on the C=C-group, the higher the selectivity to the unsaturated alcohol [see also (27)]. The adsorption through the carbonyl group becomes more abundant with increasing sterical hindrance of the olefinic group. The catalyst promoted by iron most clearly illustrates this phenomenon. In the absence of substituents on the olefinic group, the PtFe catalyst shows a quite low activity and selectivity toward the formation of the unsaturated alcohol. As soon as a methyl group is present on the olefinic group. PtFe becomes a good or even the best catalyst for the selective hydrogenation of the carbonyl group.

The presence of one or two methyl substituents on either the olefinic or the carbonylic group has a strong influence on the activity and selectivity. Kraus (25) and Simonikova *et al.* (26) considered only the electronic effects as origin of the substitutional effects. According to their observations, activity effects as result of substitution in the hydrogenation of the *isolated* olefinic or carbonylic groups are practically the same. However, the pronounced differences in selectivity observed in the hydrogenation reactions of methacrolein (a methyl group on the internal olefinic carbon atom) and methyl vinyl ketone (a methyl group on the carbonylic carbon atom) lead to the conclusion that the steric effects prevail.

Although a quantitative analysis of the changes in activity is not possible, a few qualitative trends can be formulated: (i) Whatever substitution there is on either the olefinic or carbonylic group, the reactivity of that specific group decreases. (ii) The systematic differences in the rates of hydrogenation of crotonaldehyde and meth-

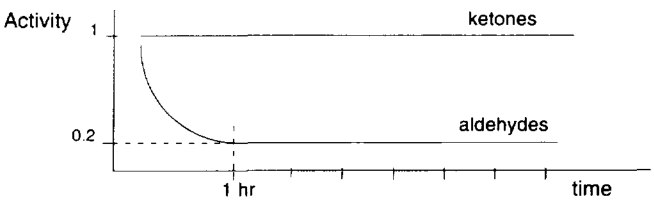


FIG. 4. Typical course of deactivation by self-poisoning in the hydrogenation of α,β-unsaturated ketones and α,β-unsaturated aldehydes.

acrolein suggest that the adsorption through the olefinic as well as through the carbonylic bond is sterically easier with the first molecule.

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