

Metal-Support Effects on the Intramolecular Selectivity of Crotonaldehyde Hydrogenation over Platinum

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The vapor-phase hydrogenation of crotonaldehyde (CROALD) was studied at low temperature and low conversions over Pt powder and Pt dispersed on SiO₂, η -Al₂O₃, and TiO₂ after either a high- or a low-temperature reduction, HTR and LTR, respectively. The hydrogenation of butyraldehyde (BUTALD) and crotyl alcohol (CROALC) to butanol (BUTNOL) and the isomerization of CROALC to BUTALD were also investigated to obtain additional information about this network of reactions. The typical Pt catalysts produced 100% BUTALD, as expected from previous studies of CROALD and the awareness of the high hydrogenation activity of Pt for C=C double bonds. However, the TiO₂-supported Pt produced both CROALC and BUTNOL, and the best catalyst, (HTR) Pt/TiO₂, gave a selectivity of 37% CROALC with no BUTNOL formation. In addition to this marked enhancement in selectivity, the turnover frequencies on the (HTR) Pt/TiO₂ samples, based on sites counted by hydrogen chemisorption near reaction temperatures, were more than an order of magnitude higher than the catalysts displaying normal adsorption behavior. Activation energies were somewhat higher on the Pt/TiO₂ catalysts, however. This behavior is very similar to that observed previously for CO and acetone hydrogenation over these same catalysts, and it is consistent with the proposal that sites created at the Pt-titania interface are responsible for the activation of carbonyl bonds. Previous studies of liquid-phase hydrogenation of CROALD and other molecules with conjugated C=C and C=O double bonds support this model and indicate that a 1,4 diadsorbed species, rather than 1,2 and 3,4 diadsorbed species (counting the oxygen atom as 1), is formed in polar solvents. By analogy, defect sites on the titania at the metal-support interface may interact with the O atom, polarize the C=O bond, and favor this intermediate which can react with hydrogen to give CROALC. © 1989 Academic Press, Inc.

INTRODUCTION

The use of certain supports such as TiO₂ has been clearly shown to markedly enhance the rate of CO hydrogenation over Group VIII metals (1-4). However, TiO₂ has not produced such rate increases for the hydrogenation of C=C double bonds or aromatic rings (5-8), and significant decreases have been reported in rates of hydrogenolysis over TiO₂-supported metals (9, 10). With an awareness of this behavior in mind, we posed the question whether the metal-support effect responsible for activation of the CO molecule might be utilized to activate carbonyl bonds in general, and we began a program to obtain an answer by

choosing acetone hydrogenation over Pt to study as a probe reaction. Very large increases in both turnover frequencies and specific activities could indeed be obtained with TiO₂, and the kinetic trends observed were very similar to those found for methanation (11).

With this confirmation of our premise, the more challenging problem of selective intramolecular hydrogenation was then addressed, and we wondered whether this affinity for activating carbonyl bonds could be utilized to favor their hydrogenation in a molecule also containing C=C double bonds and/or an aromatic ring. The capability of being able to preferentially hydrogenate carbonyl bonds rather than unsaturated C=C bonds within a molecule could have an important role both in the improvement

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of current industrial hydrogenation processes and in the future production of specialty chemicals. This paper reports our first test of this hypothesis—the hydrogenation of crotonaldehyde ($\text{CH}_3\text{—CH=CH—CH=O}$)—to determine if the normal high selectivity ($\sim 100\%$) over Pt to butyraldehyde could be shifted toward crotyl alcohol by selectively activating the carbonyl bond over TiO_2 -supported Pt. To achieve this capability with such a conjugated double bond is a difficult task in organic catalysis (12).

EXPERIMENTAL

The support materials used in this study were SiO_2 (Davison Grade 57, $220 \text{ m}^2/\text{g}$), $\eta\text{-Al}_2\text{O}_3$ (Exxon Research and Eng. Co., $245 \text{ m}^2/\text{g}$), and TiO_2 (Degussa P25—80% anatase and 20% rutile, $50 \text{ m}^2/\text{g}$). Details of the catalyst preparation procedures have been given previously along with a description of the high-vacuum systems used for chemisorption measurements (13–15).

Approximately 1 g of catalyst was placed in a Pyrex adsorption cell and each sample was reduced in H_2 using pretreatment A (1 h at 723 K), B (2 h at 473 K), or C (1 h at 773 K) according to the procedures itemized elsewhere (15). Platinum supported on $\eta\text{-Al}_2\text{O}_3$ and SiO_2 was subjected to pretreatment A while either pretreatment B or C was used for the Pt/ TiO_2 catalysts. The low-temperature reduction at 473 K is designated LTR while the high-temperature reduction at 773 K is designated HTR. The 0.7% Pt/ SiO_2 sample was calcined in 20% O_2 at 673 K at 1 h prior to pretreatment A. The high-purity Pt powder was calcined in 20% O_2 –80% He at 673 K for 1 h and then subjected to pretreatment C, and the Pt powder used in the physical mixture was similarly treated. However, since a second adsorption measurement was performed, it was again reduced in 20% H_2 –80% He for 1 h at 773 K and evacuated at 723 K for 1 h to obtain a clean surface. Irreversible hydrogen adsorption on pure SiO_2 , $\eta\text{-Al}_2\text{O}_3$, and TiO_2 is zero at room temperature, so the

saturation hydrogen coverages on Pt were measured by extrapolating the isotherms obtained between 40 and 200 Torr to zero pressure (15).

The vapor-phase hydrogenation experiments were performed in an atmospheric microreactor system described in detail elsewhere (16). The amount of catalyst loaded into the glass reactor was such as to keep the number of surface Pt atoms (Pt_s) in the reactor typically between 1 and $4 \mu\text{mol}$, based on saturation hydrogen coverages using an adsorption stoichiometry of $\text{H}_{\text{ad}}/\text{Pt}_s = 1$. The reactor was immersed in a fluidized sandbath (Tecam SBS-4) equipped with a temperature controller (West 400), and UHP hydrogen (99.999%) was further purified by passage through an Oxytrap (Alltech Associates). The gas flow rate was measured by a calibrated mass flowmeter (Teledyne Hastings-Raydist). Crotonaldehyde (CROALD, >99.5% purity, Fluka), butyraldehyde (BUTALD, 99% purity, Aldrich), and crotyl alcohol (CROALC, 97% purity, Sigma) were used as received in the hydrogenation reaction. Crotonaldehyde was introduced into the reactor system by a calibrated 5- cm^3 syringe pump (Sage Instruments Model 341A) and vaporized in the preheated reactor inlet line. Total flow rates were typically 20.4 cm^3 (STP) min^{-1} . CROALD and the products from hydrogenation—butyraldehyde, crotyl alcohol, and butanol (BUTNOL)—were analyzed by an H-P 700-00 gas chromatograph with a TC detector using an 8-ft Carbowax 20M column with an 80/100 mesh size. The absence of any diffusional limitations was confirmed by the application of the Weisz criterion (17).

Each catalyst was reduced *in situ* in 50 cm^3 (STP) min^{-1} H_2 for 1 h prior to the kinetic run. Activity measurements were done in a sequence of increasing temperature (313–373 K), decreasing temperature back to the initial temperature, and repeating the sequence of increasing temperature measurements. A bracketing technique was followed during the measurement of activ-

TABLE 1
Characterization of Platinum Catalysts by H₂ Chemisorption

| Catalyst | Precursor | Preparation method | H ₂ uptake (μmol/g) | H/Pt | d ^c (nm) |
|--|---|--------------------|--------------------------------|---------|---------------------|
| 0.7% Pt/SiO ₂ | Pt(NH ₃) ₄ Cl ₂ | IE ^a | 10.1 | 0.56 | 2.0 |
| 5% Pt/SiO ₂ | H ₂ PtCl ₆ · 6H ₂ O | IW ^b | 36.0 | 0.28 | 4.0 |
| 0.6% Pt/SiO ₂ | (NH ₃) ₂ Pt(NO ₂) ₂ | IW | 2.0 | 0.13 | 8.7 |
| 2.1% Pt/η-Al ₂ O ₃ | H ₂ PtCl ₆ · 6H ₂ O | IW | 15.7 | 0.29 | 3.9 |
| 0.2% Pt/TiO ₂ (LTR) | H ₂ PtCl ₆ · 6H ₂ O | IW | 5.9 | 1.15 | 1.1 |
| 0.2% Pt/TiO ₂ (HTR) | H ₂ PtCl ₆ · 6H ₂ O | IW | 0.2 | (0.04) | — |
| 0.4% Pt/TiO ₂ (LTR) | (NH ₃) ₂ Pt(NO ₂) ₂ | IW | 7.0 | 0.68 | 1.7 |
| 1.9% Pt/TiO ₂ (LTR) | H ₂ PtCl ₆ · 6H ₂ O | IW | 36.7 | 0.75 | 1.5 |
| 1.9% Pt/TiO ₂ (HTR) | H ₂ PtCl ₆ · 6H ₂ O | IW | 0.4 | (0.008) | — |
| 4.6% Pt/TiO ₂ (LTR) | H ₂ PtCl ₆ · 6H ₂ O | IW | 57.4 | 0.49 | 2.3 |
| 4.6% Pt/TiO ₂ (HTR) | H ₂ PtCl ₆ · 6H ₂ O | IW | 0.3 | (0.004) | — |
| Pt powder | | | 2.0 | 0.0008 | 1400 |
| Pt powder + TiO ₂ (phys. mix.) | | | 1.9 | | — |

^a Ion exchange.

^b Incipient wetness.

^c Ave. Pt crystallite diameter, d (nm) = 1.13/(H/Pt).

ity at each temperature which consisted of a 30-min reaction period followed by regeneration of the catalyst under H₂ for 25 min at the next temperature. The activity maintenance studies were conducted under continuous flow conditions.

RESULTS

The amounts of hydrogen adsorbed by the Pt catalysts after a standard pretreatment procedure, but prior to the kinetic study, are listed in Table 1. In the last two columns of Table 1, the apparent dispersions (fractions exposed) and the calculated surface-weighted average crystallite sizes are listed. For the (HTR) Pt/TiO₂ samples, this estimate is not representative of the particle size as TEM studies on similar catalysts have shown that negligible sintering of Pt occurs during HTR (18). The decrease is due to coverage of the Pt surface by migrating TiO_x species (19).

The initial activities and the selectivity behavior of the supported Pt catalysts under similar conditions are listed in Table 2. These data were obtained after preheating the catalyst in the reactor, cooling down in

pure hydrogen to the indicated reaction temperature, and then allowing the reactant mixture to flow over the catalyst for 30 min before analysis of the products. Hydrogenation of CROALD over the SiO₂- and Al₂O₃-supported catalysts produced BUTALD with 100% selectivity. The unsupported Pt powder and the physical mixture of Pt powder and TiO₂ behaved similarly and also gave only BUTALD at lower conversions, but the formation of the secondary hydrogenation product, BUTNOL, began to occur at high conversions. However, a noticeable difference in the selectivity was observed with TiO₂-supported Pt. These catalysts produced significant amounts of CROALC in addition to BUTALD and BUTNOL during the initial hydrogenation of CROALD. The selectivity of the (LTR) Pt/TiO₂ catalysts for preferential hydrogenation of the C=O bond, defined as (mol CROALC formed/mol CROALD reacted), ranged from 6 to 14%. All the samples prepared from the Pt chloride precursor showed similar selectivity (13–14%) for the formation of CROALC, but the (LTR) Pt/TiO₂ catalyst prepared

TABLE 2
Initial Activity and Selectivity of Supported Platinum Catalysts during Crotonaldehyde Hydrogenation
($P = 1$ atm; $H_2/CROALD = 22.7$)

| Catalyst | Pre-treatment ^a | Conversion (%) | T (K) | Initial activity ($\mu\text{mol CROALD}/\text{s} \cdot \text{g Pt}$) | TOF ^b (s^{-1}) | Selectivity (mol%) ^c | | |
|---|----------------------------|----------------|-------|--|--------------------------------------|---------------------------------|--------|--------|
| | | | | | | BUTALD | CROALC | BUTNOL |
| 0.7% Pt/SiO ₂ | A | 7 | 308 | 158.7 | 0.056 | 100 | 0 | 0 |
| 5% Pt/SiO ₂ | A | 20 | 319 | 63.4 | 0.044 | 100 | 0 | 0 |
| 0.6% Pt/SiO ₂ | A | 17 | 319 | 30.7 | 0.046 | 100 | 0 | 0 |
| 2.1% Pt/ η -Al ₂ O ₃ | A | 10 | 317 | 70.3 | 0.047 | 100 | 0 | 0 |
| 2.1% Pt/ η -Al ₂ O ₃ | A | — | 318 | 10.5 | 0.007 | 100 | 0 | 0 |
| 0.2% Pt/TiO ₂ (LTR) | B | 30 | 318 | 324.5 | 0.063 | 69.7 | 13.7 | 16.6 |
| 0.4% Pt/TiO ₂ (LTR) | B | 15 | 308 | 74.2 | 0.021 | 84.3 | 6.2 | 9.5 |
| 0.4% Pt/TiO ₂ (LTR) + Cl | B | 57 | 318 | 340 | — | 100 | 0 | 0 |
| 1.9% Pt/TiO ₂ (LTR) | B | 19 | 317 | 112.4 | 0.029 | 79.0 | 12.6 | 8.4 |
| 4.6% Pt/TiO ₂ (LTR) | B | 30 | 319 | 60.9 | 0.024 | 85.8 | 14.2 | 0 |
| 0.2% Pt/TiO ₂ (HTR) | C | 14 | 307 | 147.0 | 0.74 | 70.9 | 19.9 | 9.2 |
| 0.4% Pt/TiO ₂ (HTR) | C | 7 | 307 | 29.0 | 0.29 | 83.4 | 3.8 | 12.8 |
| 0.4% Pt/TiO ₂ (HTR) + Cl | C | 16 | 317 | 93.0 | — | 100 | 0 | 0 |
| 1.9% Pt/TiO ₂ (HTR) | C | 12 | 318 | 70.5 | 1.68 | 62.8 | 37.2 | 0 |
| 4.6% Pt/TiO ₂ (HTR) | C | 53 | 319 | 108.9 | 8.34 | 52.5 | 0 | 47.5 |
| Pt powder | C | 88 | 318 | 0.57 | 0.143 | 92.2 | 0 | 7.8 |
| Pt powder | C | 32 | 328 | 0.22 | 0.052 | 100 | 0 | 0 |
| Pt powder + TiO ₂ | C | 20 | 314 | 0.39 | 0.102 | 100 | 0 | 0 |

^a See text.

^b Molecule C₄H₆O (CROALD) reacted $\cdot \text{s}^{-1} \cdot \text{Pt}_c^{-1}$.

^c Butyraldehyde (BUTALD), crotyl alcohol (CROALC), butanol (BUTNOL).

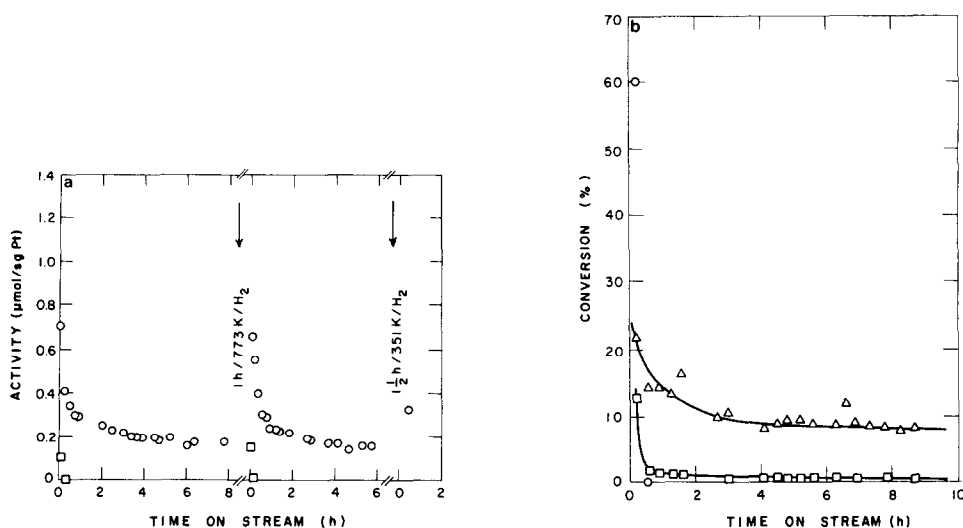


FIG. 1. (a) Activity maintenance for crotonaldehyde hydrogenation over Pt powder: \circ , butyraldehyde formation; \square , butanol formation ($T = 352$ K, $P_T = 0.1$ MPa, $H_2/CROALD = 22.7$). Arrows represent regeneration under conditions stated in text. (b) Activity maintenance for crotonaldehyde hydrogenation over (HTR) 0.2% Pt/TiO₂: Δ , conversion to butyraldehyde; \square , conversion to crotyl alcohol; \circ , conversion to butanol ($T = 356$ K, $P_T = 0.1$ MPa, $H_2/CROALD = 22.7$).

from a nitrite precursor exhibited a lower selectivity of 6%. After the Cl-containing Pt/TiO₂ samples were subjected to a HTR step, there were significant increases in the selectivity toward hydrogenation of the C=O bond; however, a decrease of a factor of 2 occurred with the catalyst prepared from the nitrite precursor. The specific activities for the hydrogenation of CROALD were comparable for all the supported catalysts having normal adsorption behavior and turnover frequencies between 310 and 320 K were routinely $3\text{--}10 \times 10^{-2} \text{ s}^{-1}$.

Representative activity maintenance profiles are shown in Fig. 1a for the unsupported Pt powder and in Fig. 1b for the (HTR) 0.2% Pt/TiO₂ catalysts. It is apparent that there is substantial deactivation of the catalyst at higher temperatures and conversions as a function of time on stream and that the sites favoring hydrogenation of the C=O bond appear to be deactivated faster than those responsible for olefinic bond hydrogenation.

The hydrogenation activities at 353 K and the apparent activation energies for the

overall conversion of CROALD are listed in Table 3. As shown in Fig. 2, although there was some variation in the data as repeated temperature cycles were conducted (the results for the (HTR) Pt/TiO₂ sample include four such cycles), there was no trend of deactivation observed indicating the effectiveness of the regeneration period in H₂. The average apparent activation energy for the titania-supported samples above 330 K is about 2–3 kcal/mol greater than those for the silica- and alumina-supported samples. Because of the deactivation and typical low selectivity for the hydrogenation of the C=O bond, it was not possible to obtain separate apparent activation energies for the formation of BUTALD and CROALC except for the (HTR) 1.9% Pt/TiO₂ sample, for which the activation energies for BUTALD and CROALC formation were 6 and 10 kcal/mol, respectively.

Since the Pt/TiO₂ catalysts prepared from H₂PtCl₆ had the highest selectivity for hydrogenation of the C=O functional group, the effect of chloride was examined

TABLE 3

Overall Crotonaldehyde Hydrogenation Rates over Supported Platinum Catalysts
($T = 353 \text{ K}$, $P_{\text{total}} = 1 \text{ atm}$, $\text{H}_2/\text{CROALD} = 22.7$)

| Catalyst | Conversion range (%) | Activity ($\mu\text{mol/g Pt} \cdot \text{s}$) | TOF ^a ($\text{s}^{-1} \times 10^2$) | E_{act} (Kcal/mol) |
|---|----------------------|--|--|-----------------------------|
| 0.7% Pt/SiO ₂ | 8–13 | 269 ± 17 | 9.3 ± 0.6 | 3 |
| 5% Pt/SiO ₂ | 18–35 | 94 ± 6 | 6.5 ± 0.4 | 3 |
| 0.6% Pt/SiO ₂ | 15–32 | 28 ± 2 | 6.9 ± 0.6 | 6 |
| 2.1% Pt/ η -Al ₂ O ₃ | 4–9 | 49 | 3.3 | 4 |
| 2.1% Pt/ η -Al ₂ O ₃ | 4–10 | 54 ± 3 | 3.6 ± 0.2 | 4 |
| 0.2% Pt/TiO ₂ (LTR) | 6–27 | 150 ± 20 | 2.5 ± 0.3 | 7 |
| 0.4% Pt/TiO ₂ (LTR) | 3–9 | 32 ± 5 | 0.9 ± 0.2 | 7 |
| 1.9% Pt/TiO ₂ (LTR) | 5–31 | 108 ± 16 | 2.8 ± 0.4 | 8 |
| 4.6% Pt/TiO ₂ (LTR) | 17–47 | 106 ± 18 | 4.6 ± 0.8 | 8 |
| 0.2% Pt/TiO ₂ (HTR) | 4–13 | 95 ± 10 | 48 ± 5 | 6 |
| 0.4% Pt/TiO ₂ (HTR) | 1–5 | 20 ± 3 | 20 ± 3 | 5 |
| 1.9% Pt/TiO ₂ (HTR) | 5–15 | 63 ± 11 | 150 ± 26 | 7 |
| 4.6% Pt/TiO ₂ (HTR) | 3–10 | 16 ± 6 | 133 ± 50 | 5 |
| Pt powder | 14–36 | 0.14 ± 0.02 | 3.5 ± 0.4 | 4 |
| Pt powder + TiO ₂ (phys. mix.) | 5–10 | 0.08 ± 0.02 | 2.1 ± 0.5 | 4 |

^a Molecule C₄H₆O reacted · s⁻¹ · Pt_s⁻¹.

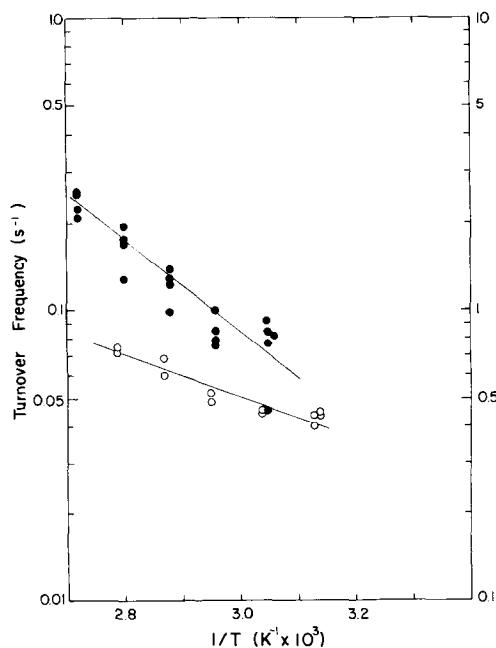


FIG. 2. Arrhenius plots for crotonaldehyde hydrogenation (molecule C₄H₆O · s⁻¹ · Pt_{surf}⁻¹) over Pt Catalysts ($P_{\text{Total}} = 0.1 \text{ MPa}$, $\text{H}_2/\text{CROALD} = 22.7$): (HTR) 1.9% Pt/TiO₂, ●; 5.0% Pt/SiO₂, ○.

by adding HCl to the 0.4% Pt/TiO₂ sample prepared from the nitrite precursor, and the results are also listed in Table 2. The amount of HCl added, 400 $\mu\text{mol Cl/g cat.}$ ($\text{Cl/Pt} = 19.5$), was that required to saturate the TiO₂ surface based on the adsorption measurements of Siriwardane and Wightman (20). Compared to the Cl-free sample, the sample to which HCl was added showed no activity for C=O bond hydrogenation; however, a higher activity for C=C bond hydrogenation was obtained.

To gain more information about the reaction pathways during CROALD hydrogenation, hydrogenation of BUTALD and CROALC was also studied. The time-dependent activity profiles during BUTALD hydrogenation are shown in Figs. 3a and 3b, and they reveal that the Pt/SiO₂ and (HTR) Pt/TiO₂ catalysts were fairly stable but Pt/Al₂O₃ and (LTR) Pt/TiO₂ showed rapid initial deactivation. No isomerization to BUTALD was detected. A comparison of the kinetic behavior of these catalysts is

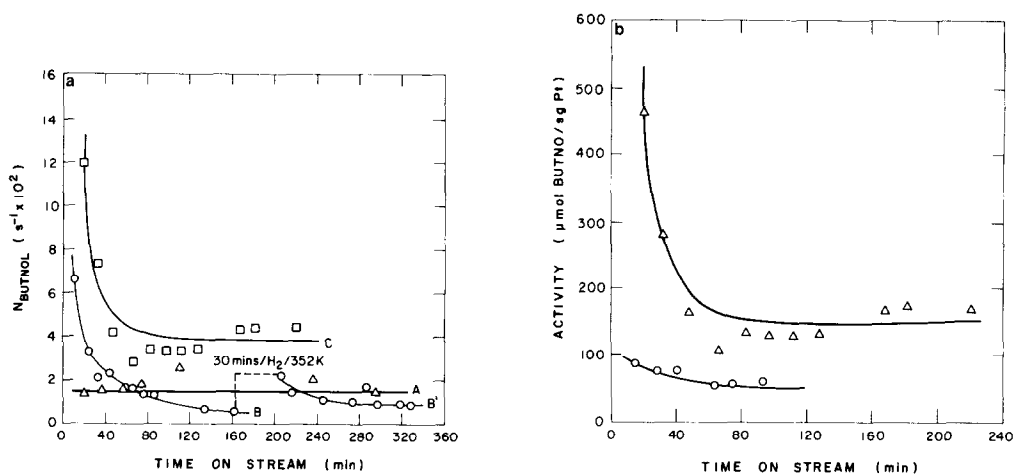


FIG. 3. Activity profile for butyraldehyde hydrogenation to butanol as a function of time on stream ($\text{H}_2/\text{BUTALD} = 24.5$, $P_T = 0.1$ MPa): (A) 0.7% Pt/SiO₂, $T = 323$ K; (B) 2.1% Pt/ η -Al₂O₃, $T = 321$ K; (B') 2.1% Pt/ η -Al₂O₃, $T = 352$ K; (C) 1.9% Pt/TiO₂ (LTR), $T = 342$ K. (b) Activity profile for butyraldehyde hydrogenation to butanol over titania-supported Pt as a function of time on stream ($\text{H}_2/\text{BUTALD} = 24.5$, $P_T = 0.1$ MPa): Δ , 1.9% Pt/TiO₂ (LTR), $T = 342$ K; \circ , 1.9% Pt/TiO₂ (HTR), $T = 341$ K.

made in Table 4. After HTR the activity (per gram Pt) of the Pt/TiO₂ catalyst decreased about threefold compared to that after the LTR pretreatment, but the TOF increased markedly while the activation energy remained constant at 10 kcal/mol.

During hydrogenation of CROALC two products—BUTALD and BUTNOL—were obtained under the reaction conditions used in this study. A comparison of the profiles for isomerization activity versus time over the three catalysts exhibiting normal adsorption behavior is shown in Fig. 4a. Under H₂ the (LTR) Pt/TiO₂ catalyst showed no loss in isomerization activity of CROALC to BUTALD over a period of approximately 2 h whereas the silica- and alumina-supported catalysts deactivated in comparable fashion. The formation of BUTNOL over the three catalysts as a function of time on stream is shown in Fig. 4b, and a comparison of the activities of the Pt/TiO₂ after LTR and HTR pretreatments is shown in Fig. 5. For the isomerization reaction the HTR sample did not show a decrease in activity whereas hydrogenation to BUTNOL declined quite noticeably. The

catalytic activities and selectivities of the supported Pt catalysts during CROALC hydrogenation are listed in Table 5. For the isomerization of CROALC to BUTALD the SiO₂-supported catalyst is about three times more active than the alumina- and titania-supported catalysts. No isomerization activity of CROALC to BUTALD was observed at these temperatures under He in the absence of H₂.

The most important results are summarized as follows: (i) only the TiO₂-supported

TABLE 4
Butyraldehyde Hydrogenation to Butanol over Supported Platinum Catalysts
($T = 353$ K, $P_{\text{total}} = 1$ atm, $\text{H}_2/\text{BUTALD} = 24.5$)

| Catalyst | Steady-state activity ^a ($\mu\text{mol BUTALD}/$ $\text{s} \cdot \text{g Pt}$) | TOF (s^{-1}) | E_{act} (Kcal/mol) |
|---|---|----------------------------|--------------------------------|
| 0.7% Pt/SiO ₂ | 147 ^a | 0.051 | — |
| 2.1% Pt/ η -Al ₂ O ₃ | 147 ^a | 0.098 | — |
| 1.9% Pt/TiO ₂ (LTR) | 386 | 0.10 | 10 |
| 1.9% Pt/TiO ₂ (HTR) | 110 | 2.6 | 10 |

^a Extrapolated value using $E = 10$ kcal/mol and activity after 160 min on stream.

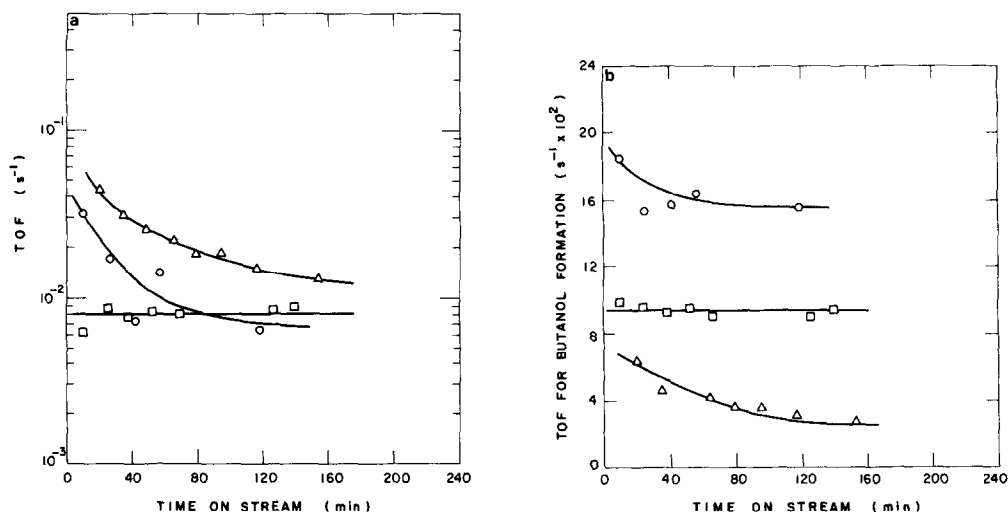


FIG. 4. Activity profile (molecule \cdot s $^{-1}$ \cdot Pt $_s$) for the isomerization of crotyl alcohol to butyraldehyde ($H_2/CROALC = 31$, $P_T = 0.1$ MPa): Δ , 0.7% Pt/SiO $_2$, $T = 356$ K; \circ , 2.1% Pt/ η -Al $_2$ O $_3$, $T = 374$ K; \square , 1.9% Pt/TiO $_2$ (LTR), $T = 345$ K. (b) Activity profile for the hydrogenation of crotyl alcohol to butanol ($H_2/CROALC = 31$, $P_T = 0.1$ MPa): \circ , 2.1% Pt/ η -Al $_2$ O $_3$, $T = 374$ K; \square , 1.9% Pt/TiO $_2$ (LTR), $T = 345$ K; Δ , 0.7% Pt/SiO $_2$, $T = 356$ K.

Pt catalysts showed any selectivity toward hydrogenation of the C=O bond rather than the C=C bond in CROALD; (ii) the selectivity toward the hydrogenation of the C=O is higher for the best Pt/TiO $_2$ catalysts prepared from a chloride precursor; (iii) isomerization of crotyl alcohol to butyraldehyde in the presence of hydrogen is approximately three times faster on silica-supported Pt than on alumina- and titania-supported Pt; (iv) the initial rate of hydrogenation of CROALC is greater than the rate of isomerization over all the catalysts and is an order of magnitude higher on the Pt/Al $_2$ O $_3$ and (LTR) Pt/TiO $_2$ catalysts; (v) certain catalysts deactivate significantly during the course of these reactions whereas other exhibit good stability.

DISCUSSION

On the basis of our previous studies of CO hydrogenation over noble metals which showed that the use of certain supports, especially TiO $_2$, could markedly enhance specific activity (1-4), a model was proposed invoking special sites at the metal-support interface (21). Recently, this heuristic con-

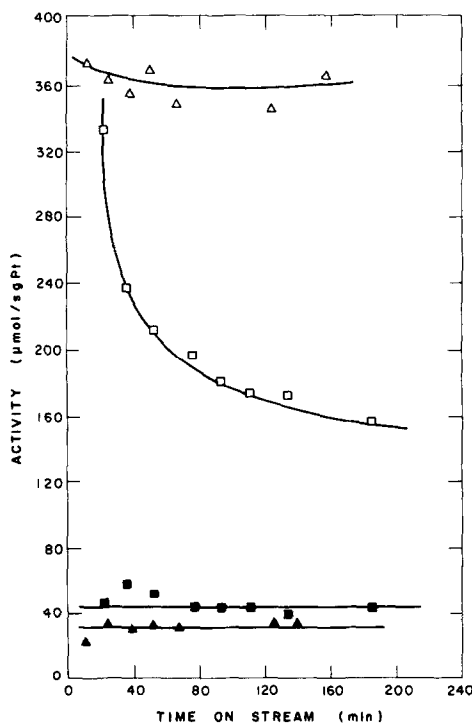


FIG. 5. Activity profile for crotyl alcohol conversion over 1.9% Pt/TiO $_2$ ($H_2/CROALC = 31$, $P_T = 0.1$ MPa): At 337 K after (HTR) pretreatment, \square , \blacksquare ; at 345 K after (LTR) pretreatment, Δ , \blacktriangle ; BUTNOL formation, open symbols; BUTALD formation, solid symbols.

TABLE 5

Hydrogenation of Crotyl Alcohol over Supported Pt Catalysts
($T = 353$ K, $H_2/CROALC = 31$, $P_{total} = 1$ atm)

| Catalyst | Isomerization to BUTALD | | | Hydrogenation to BUTNOL | | |
|---|--|---|-----------------------------|--|---|-----------------------------|
| | Activity ^a ($\mu\text{mol BUTALD}/$ $\text{s} \cdot \text{g Pt}$) | TOF ^a (s^{-1}) | E_{act} (Kcal/ mol) | Activity ^a ($\mu\text{mol BUTALD}/$ $\text{s} \cdot \text{g Pt}$) | TOF ^a (s^{-1}) | E_{act} (Kcal/ mol) |
| 0.7% Pt/SiO ₂ | 90 | 0.030 | 7 | 150 | 0.53 | 2 |
| 2.1% Pt/ η -Al ₂ O ₃ | 15 | 0.010 | 4 | 199 | 0.133 | 3 |
| 1.9% Pt/TiO ₂ (LTR) | 39 | 0.010 | — | 401 | 0.104 | — |
| 1.9% Pt/TiO ₂ (HTR) | 63 | 1.50 | 6 | 275 | 6.5 | 3 |

^a Initial activity after 40 min on stream adjusted to 353 K.

cept of carbonyl bond activation was further tested by us during a kinetic study of acetone hydrogenation to isopropanol over this family of Pt catalysts, and the 500-fold enhancement in turnover frequencies over (HTR) Pt/TiO₂ catalysts provided additional support for this model (11). Not only to utilize a more demanding test of the hypothesis that carbonyl bonds could be selectively activated by appropriate metal-support combinations, but also to explore controlling the hydrogenation of specific bonds within a molecule, the reaction of crotonaldehyde over Pt in a H₂-rich environment was examined. Selective addition of hydrogen to the carbonyl bond produces crotyl alcohol whereas hydrogenation only of the C=C double bond gives butyraldehyde and complete hydrogenation yields butanol. In addition, isomerization of CROALC to BUTALD can occur.

The most important result of this study is the marked enhancement in activity for hydrogenation of the carbonyl bond in CROALD when titania is used as a support. It increases from a nondetectable level on SiO₂- and Al₂O₃-supported Pt to a specific activity comparable to that for C=C double bond hydrogenation, particularly on the (HTR) Pt/TiO₂ catalysts. This produced an increase in CROALC selectivity from 0 to 37% over the best catalyst. The significance of this alteration can be better understood

by comparing the results in Table 2 with those of previous studies of CROALD hydrogenation over solid metal catalysts (22–34), which are summarized in Table 6. The first conclusion that can be reached from reviewing Table 6 is that few catalysts have given a high selectivity to CROALC. The second is that Pt-only catalysts would not be expected to be selective for CROALC formation. The third conclusion is that Os is the metal providing the highest selectivity, which is consistent with studies of carbonyl bond hydrogenation in homogeneous systems that have also shown Os-containing clusters to be the best catalysts, with a maximum selectivity to CROALC of 50% being reported by Sanchez-Delgado *et al.* (35). During the course of this study, Wismeijer *et al.* published two papers showing that TiO₂-supported Ru had greater activity and selectivity than SiO₂-supported Ru for C=O bond hydrogenation, compared to C=C bond hydrogenation, but selectivities for CROALC during CROALD hydrogenation were not reported (22, 23).

An α , β -unsaturated carbonyl compound has a carbon-carbon double bond conjugated with a carbon-oxygen double bond. Selective intramolecular hydrogenation of only the carbonyl functional group in an α , β -unsaturated aldehyde is a challenging task, as discussed by Jenck and Germain (12). One reason is provided by the ther-

TABLE 6
Activity and Selectivity of Crotonaldehyde Hydrogenation over Transition Metals, $P_{H_2} \equiv 0.1$ MPa

| Catalyst | Phase | T (K) | Conversion (%) | TOF (s ⁻¹) | Activity ^a | | Selectivity (mol%) | | | Ref. |
|---|-------|-------|-----------------|------------------------|------------------------------|-----------------------------|--------------------|--------|--------|------|
| | | | | | (μ mol/ s · g metal) | (μ mol/ s · g cat.) | BUTALD | CROALC | BUTNOL | |
| 5% Ru/SiO ₂ | L | 303 | — | 0.0014 ^b | 13.9 ^c | 0.70 ^c | — | — | — | 22 |
| 1% Ru/TiO ₂ | L | 303 | — | 0.011 ^b | 107 ^c | 1.1 ^c | — | — | — | 22 |
| 16.67% NiO/Al ₂ O ₃ | G | 353 | 100 | — | — | — | 14 | 0 | 86 | 24 |
| 22.5% CuO/Al ₂ O ₃ | G | 353 | 10 | — | — | 0.012 | 100 | 0 | 0 | 24 |
| 21% NiO, 10% CuO/Al ₂ O ₃ | G | 353 | 100 | — | — | — | 12 | 54 | 33 | 24 |
| Ni-Al-Cu | L | 358 | 13 | — | — | 0.9 | 64 | 5 | 31 | 25 |
| Os/Al ₂ O ₃ | L | 293 | — | — | — | — | — | 80 | — | 26 |
| Os/ZnO | L | 293 | — | — | — | — | — | — | — | 26 |
| Ru/Al ₂ O ₃ | L | 293 | — | — | — | — | — | 13 | — | 26 |
| Ru/ZnO | L | 293 | — | — | — | — | — | 22 | — | 26 |
| Rh/ZnO | L | 293 | — | — | — | — | — | 11 | — | 26 |
| Ru black | L | 293 | 77 | 0.054 | 87 ^c | — | 60 | 10 | 29 | 27 |
| Ru black-Al ₂ O ₃ | L | 293 | 78 | — | 30 ^c | — | 61 | 13 | 26 | 27 |
| Ru black-ZnO | L | 293 | 75 | — | 38 ^c | — | 37 | 24 | 39 | 27 |
| Pd black | L | 293 | — | 0.033 | 24 ^c | — | 100 | 0 | 0 | 28 |
| Pd black-B ₂ O ₃ | L | 293 | — | — | 27 ^c | — | 100 | 0 | 0 | 28 |
| Pd-SiO ₂ | L | 293 | — | — | 24 ^c | — | 100 | 0 | 0 | 28 |
| Pd-Al ₂ O ₃ | L | 293 | — | — | 26 ^c | — | 100 | 0 | 0 | 28 |
| Pd-MgO | L | 293 | — | — | 68 ^c | — | 100 | 0 | 0 | 28 |
| Pd-Fe ₂ O ₃ | L | 293 | — | — | 74 ^c | — | 100 | 0 | 0 | 28 |
| Pd-ZnO | L | 293 | — | — | 89 ^c | — | 100 | 0 | 0 | 28 |
| Cu/Cr ₂ O ₃ | G | 313 | 26 | — | — | — | 88 | 6 | 6 | 29 |
| Ru/C | L | 308 | — | — | — | — | 25 | 25 | 50 | 30 |
| Pt/C, FeCl ₂ , ZnAc ₂ | L | — | 91 ^d | — | — | — | — | — | — | 31 |
| Re/pyridine | L | 363 | 96 ^e | — | — | — | — | — | — | 31 |
| 1% Pt/SiO ₂ | G | 433 | — | — | — | — | 100 | 86 | — | 32 |
| 1% Pt + 0.7% Fe/SiO ₂ | G | 433 | 20 | — | 90 | 0.9 | 50 | 20 | 30 | 32 |

^a Based on CROALD consumption.

^b Assuming a dispersion of unity.

^c Based on micromoles H₂ consumed.

^d $P_{H_2} = 0.4$ MPa.

^e $P_{H_2} = 17.5$ MPa.

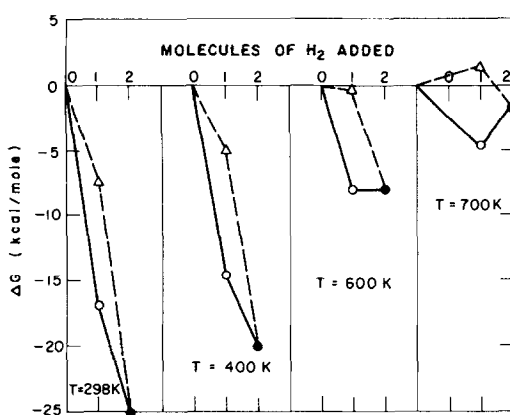


Fig. 6. Free energy change in the hydrogenation of crotonaldehyde per mole of hydrogen added: \circ , butyraldehyde; Δ , crotyl alcohol.

modynamics associated with the two pathways in the complete hydrogenation of CROALD, i.e., the formation first of BUTALD or CROALC, as shown in Fig. 6. To obtain a high selectivity to CROALC, kinetic control must be induced not only to form this product first rather than BUTALD but also to prevent it from reacting further to isomerize to BUTALD or hydrogenate to BUTALC. It is clear that BUTALD is the thermodynamically favored initial product, and the formation of BUTNOL might be expected to proceed through this route, rather than with CROALC, at the temperatures used in this study. This consideration helps explain why so few catalysts have been found to produce CROALC from CROALD with high selectivity (22–34).

Unfortunately, there have been no previous reports of specific activities (per metal surface area) or turnover frequencies (TOFs) for CROALD hydrogenation over Pt or any other metal; consequently, our TOF values appear to be the first determined for this reaction. The activity given in Table 6 for the FeSO_4 -promoted Pt/ SiO_2 catalyst was estimated from the work of Simonik and Beranek (32), the TOF values for Ru and Pd were calculated from the studies of Sokolskii and co-workers (27, 28) using their BET surface areas and assuming

site densities of 1.5×10^{19} Ru_s/m^2 and 1.2×10^{19} Pd_s/m^2 and H_2 consumptions under STP conditions, and the TOFs for the Ru catalysts examined by Wismeijer *et al.* (22) were based on the assumption of 100% dispersion. Most of the results in Table 6 are further complicated by the fact that they were obtained in the liquid phase using various solvents. Regardless, the activities per gram Pt on SiO_2 and Al_2O_3 found in our study are comparable to those per gram Ru, Pd, and Pt in Table 6, and the TOF values among the unsupported Ru and Pd and our typical Pt catalysts are surprisingly similar. The lower TOF values for the supported Ru may be a consequence of the assumption of 100% dispersion, which gives a minimum estimate.

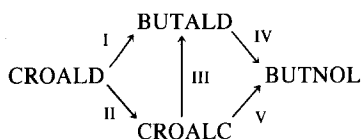
As for specific rates, there are no reported values of apparent activation energies in the literature for CROALD hydrogenation. In this study the activation energy for CROALD hydrogenation was found to lie between 3 and 8 kcal/mol. Such low activation energies are frequently encountered in alkene hydrogenation, and the activation energy has been found to decrease as the chain length of the alkene increases (36, 37). In butene hydrogenation, which is the alkene analog of CROALD, activation energies of 2–4 kcal/mol have been routinely reported over Ni and Pt catalysts (38). The lower apparent activation energies over Pt powder, Pt/ SiO_2 , and Pt/ $\eta\text{-Al}_2\text{O}_3$ are probably due to the hydrogenation of the olefinic carbon bond in CROALD being the predominant reaction pathway. Oldenburg and Rase (39) studied the vapor-phase hydrogenation of butyraldehyde over a 80% Ni/kieselguhr catalyst and reported an apparent activation energy of 7.8 kcal/mol; thus the value of 10 kcal/mol in Table 4 obtained for the Pt/ TiO_2 catalysts is reasonable in comparison. For CROALC hydrogenation a direct comparison is again not possible; however, the activation energies of 2–3 kcal/mol are the same as those for butene (38). Also, the results in Table 5 are in agreement with those of Simonik and

TABLE 7

Relative Rates for the Various Reactions Shown below
(Assuming Similar Coverages of Reactant), $T = 353$ K

| Catalyst | r_V/r_{IV} | r_{II}/r_I | $(r_{III} + r_V)/r_{II}$ | r_{IV}/r_I | r_{IV}/r_V | r_V/r_{II} | r_V/r_{III} |
|--|--------------|------------------------|--------------------------|--------------|--------------|--------------|---------------|
| 0.7% Pt/SiO ₂ | 1.0 | 0 | ∞ | 0.9 | 0.96 | ∞ | 1.8 |
| 2.1% Pt/Al ₂ O ₃ | 1.4 | 0 | ∞ | 2.1 | 0.74 | ∞ | 13 |
| 1.9% Pt/TiO ₂ (LTR) | 1.0 | 0.2 (0.4) ^a | 4.1 | 4.3 | 0.96 | 3.7 | 10 |
| 1.9% Pt/TiO ₂ (HTR) | 2.5 | 0.6 | 5.3 | 2.5 | 0.4 | 4.3 | 4.3 |

^a Assuming all BUTNOL forms via CROALC.



Beranek, who found that CROALC isomerization to BUTALD was accompanied by hydrogenation to BUTNOL over a 1% Pt, 0.7% Fe/SiO₂ catalyst (33).

The overall hydrogenation of CROALD to BUTNOL represents a complex series/parallel reaction sequence that also includes an isomerization step, as illustrated in Table 7. A complete kinetic description of this network is not available, although one effort has been made to describe it (32), and the limited kinetic data obtained here do not allow a representation of simultaneous rates. Regardless, it is worthwhile to note certain aspects of the rates in Tables 3–5, all of which have been determined at 353 K. With single-component feeds, the TOFs for the hydrogenation of CROALD, BUTALD, and CROALC are similar and typically range from 0.03 to 0.13 s⁻¹ over Pt powder and Pt on SiO₂, Al₂O₃, and (LTR) TiO₂. The TOF for isomerization is again similar over the normal Pt catalysts but is lower than that for any hydrogenation step, varying between 0.01 and 0.03 s⁻¹. The same similarity among the three hydrogenation TOFs exists for the (HTR) Pt/TiO₂ catalyst, but they are all much greater in absolute magnitude. A comparison of these relative rates over a given catalyst is provided in Table 7. The slightly lower TOF

for BUTALD formation on the (LTR) Pt/TiO₂ catalysts implies that some sites on the Pt surface may have been converted to a type capable of producing CROALC rather than BUTALD. For the (HTR) Pt/TiO₂ catalysts, the low reaction temperatures are close to that (300 K) used to measure chemisorbed hydrogen; consequently, the latter should be a good representation of sites available for the hydrogenation reactions investigated here, and the high TOF values have additional importance because they relate to sites capable of activating H₂ in the same temperature regime. These sites have a high efficiency for all the reactions studied here, yet the selectivity to CROALC can be quite significant, as shown in Table 2. Finally, the similarity among all hydrogenation rates over any given catalyst indicates the significant role that adsorption must play under reaction conditions in determining the product distribution. For example, the relative rates of steps IV and I (column 5, Table 7) indicate that adsorbed CROALD is highly favored over adsorbed BUTALD on the Pt/SiO₂ and Pt/Al₂O₃ catalysts whereas adsorption of CROALC, once formed, appears to be much more competitive with CROALD on the Pt/TiO₂ catalysts because BUTNOL is formed. This is consistent with the supposi-

tion that the strongest adsorption on the Pt will occur via the C=C double bond and that typical Pt catalysts readily hydrogenate these bonds (34, 37, 38).

It is noted that HTR does not always result in an increase in CROALC, as indicated by the 0.4% Pt/TiO₂ and 4.65 Pt/TiO₂ samples in Table 2. However, TOF values did increase markedly in both cases, and the higher activity for CROALC hydrogenation to BUTNOL is likely to be the explanation for the low selectivity to CROALC. The optimum catalyst, though, is going to be extremely dependent on the Pt-TiO_x interfacial area, and this could be the predominant factor in selectivity variability. Unfortunately, we do not yet sufficiently understand the spreading of TiO_x to control it.

It is not the intent of this paper to consider mechanistic aspects in detail; however, some discussion seems appropriate and a proposal for the role of the support can be made. The possible configurations of adsorbed CROALD and subsequent products have been described by Hubaut *et al.* (29) and Augustine (40). The relative amounts of BUTALD and CROALC can be governed by the adsorbed intermediate as 1,2 hydrogen addition (counting the oxygen atom as 1) would give the latter while 3,4 addition would produce the former in a manner analogous to the classical Horiuti-Polanyi mechanism (37). However, 1,4 adsorption can produce a facile C=C bond shift and subsequent 1,4 addition gives an enolic species, possibly a π -allylic form, whose stability on Pt appears to be favored (41), that can yield either CROALC or BUTALD. The kinetic analysis of Simonik and Beranek led them to propose that these two products originated from a common adsorbed intermediate (32). Also, Fujitsu and co-workers have shown that increasing the polarization of the carbonyl bond in aldehydes and ketones by the addition of an electron-withdrawing group to the molecule increases the rate of hydrogenation (42). Further, in aprotic solvents with a high dielectric constant, the 1,4 addition is known

to be favored, presumably because of the capability of the polar solvent to activate the carbonyl oxygen atom (40, 43).

All these results considered together are consistent with the model we have proposed for activation of carbonyl bonds on TiO₂-supported metal catalysts (11, 21), i.e., special sites are created at the metal-support interface involving either Ti³⁺ (or Ti²⁺) cations or oxygen vacancies that coordinate the oxygen atom in the C=O group and activate it. The close presence of activated hydrogen from the Pt surface provides for the facile hydrogenation of this group and does not require significant distances for H spillover (44, 45). It has now been clearly established that TiO_x species can migrate over metal surfaces under high-temperature reducing conditions (19, and references therein). Consequently, large adlineation regions can exist on both large and small metal crystallites after appropriate pretreatments. We have not observed rate enhancements in physical mixtures of Pt and TiO₂ for the hydrogenation of CO (46), acetone (11), or this reaction as clearly shown in Tables 2 and 3. Consequently, we discount the suggestion that H spillover is responsible for the higher activity (23), at least with regard to sites outside the adlineation region. The supposition that 1,4 adsorption of CROALD occurs on these interface sites is consistent with the aforementioned studies, it requires only a single Pt atom in this active site, and it explains the shift to higher CROALC selectivities. This proposal is also supported by the studies of Poltarzewski, Galvagno, and co-workers, who found that the addition of tin oxide to a Pt/nylon catalyst enhanced the selectivity to allyl alcohol in acrolein hydrogenation and to cinnamyl alcohol in cinnamaldehyde hydrogenation (36, 47). Tuley and Adams had reported earlier that the addition of Fe³⁺ to Pt black increased selectivity to cinnamyl alcohol in the latter reaction (48). In conclusion, although the results reported here do not prove our model, they are very consistent with it and provide additional evidence that it is a valid working

concept to be subjected to further tests in the future.

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