RECEIVED
JAN 22 1997
OSTI

IS-T 1779

The Selective Hydrogenation of Crotonaldehyde over Bimetallic Catalysts

by

Schoeb, Ann M.

PHD Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE
Iowa State University
Ames, Iowa 50011

Date Transmitted: October 17, 1996

MASTER

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-Eng-82.

AVAILABILITY:

To DOE and DOE contractors: Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

prices available from: (615) 576-8401
FTS: 626-8401

To the public: National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

TABLE OF CONTENTS

Preprint – Removed for separate processing.

Preprint removed for separate processing

ABSTRACT

The selective hydrogenation of crotonaldehyde has been investigated over a monometallic Pt/SiO_2 catalyst and platinum bimetallic catalysts where the second metal was either silver, copper, or tin. The effects of addition of a second metal to the Pt/SiO_2 system on the selectivity to crotyl alcohol were investigated.

The Pt-Sn bimetallic catalysts were characterized by hydrogen chemisorption, ^1H NMR and microcalorimetry. The Pt-Ag/SiO_2 and Pt-Cu/SiO_2 catalysts were characterized by hydrogen chemisorption. Pt-Sn/SiO_2 catalysts selectively hydrogenated crotonaldehyde to crotyl alcohol and the method of preparation of the these catalysts affected the selectivity. The most selective Pt-Sn/SiO_2 catalysts for the hydrogenation of crotonaldehyde to crotyl alcohol were those in which the Sn precursor was dissolved in a HCl solution. Sn increased both the rate of formation of butyraldehyde and the rate of formation of crotyl alcohol. The Pt/SiO_2, Pt-Ag/SiO_2 and Pt-Cu/SiO_2 catalysts produced only butyraldehyde.

Initial heats of adsorption (~ 90 kJ/mol) measured using microcalorimetry were not affected by the presence of Sn on Pt. We can conclude that there is no through metal electronic interaction between Pt and Sn at least with respect to hydrogen surface bonds since the Pt and Pt-Sn had similar initial heats of adsorption coupled with the invariance of the ^1H NMR Knight shift.

Selective site blocking of the low coordination edge and corner sites by Cu or Ag as well as reduction in the Pt ensemble size did not lead to the formation of crotyl alcohol as has been postulated in previous work. Also, these low coordination edge and corner sites cannot be responsible for the olefin hydrogenation activity since the TOF for Pt-Ag/SiO_2 and Pt/SiO_2 were identical. Sn addition increased the H/Surface Pt ratio. That is, Sn promotes additional hydrogen adsorption per surface Pt atom. This additional hydrogen is more weakly bound. The presence of additional adsorbed hydrogen on both Pt-Sn and Pt-Cu is correlated with the increased activity obtained for these catalyst systems relative to pure Pt and Pt-Ag. Unlike Ag and Cu, Sn is not easily reduced and this partially reduced state may be necessary for activation of the carbonyl group.

GENERAL INTRODUCTION

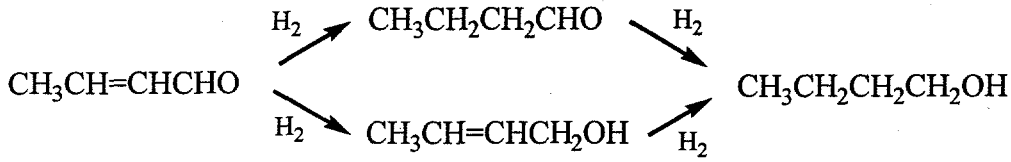
Supported bimetallic catalysts have been used extensively in industry despite the general lack of understanding of how the small metal particles interact with the reacting species. Supported bimetallic catalysts offer a variety of interesting possibilities in designing the selectivity of heterogeneous catalysts and these benefits have been exploited in numerous industrial processes. In the 1970s bimetallic catalysts such as supported platinum-rhenium and platinum-iridium replaced traditional supported platinum catalysts used in the petroleum industry. Addition of the second metal gave the catalyst higher selectivity and stability. Coking was decreased and the metallic crystallites appeared more resistant to aging (1). Other examples of bimetallic systems used in industry include the following: oxidation of ammonia over platinum-rhodium catalysts in the form of wire gauze to produce nitric oxide, platinum-rhodium catalysts is the form of wire gauze are also used in the Andrussow process (synthesis of hydrogen cyanide), three-way catalysts containing the noble metals platinum, palladium, and rhodium for the simultaneous conversion of hydrocarbons, carbon monoxide, and nitrogen oxides in automobile exhaust, and platinum-tin catalysts are used in several hydrocarbon transformation processes such as reforming of naphtha (2) and dehydrogenation of alkanes for detergent production (3).

Bimetallic catalyst particles are usually on the order of 10-50 Å in size. Due to the small size of these particles almost every metal atom is exposed to the surface. The clusters are usually supported on high surface area carriers such as silica or alumina. These supported bimetallic clusters can be prepared by impregnation of alumina or silica with an aqueous solution of the salts of the two metals of interest. After the material is dried it is placed in a stream of hydrogen at a temperature high enough to promote the reduction of the metal precursors to the metallic state.

One of the properties of the catalyst which can be influenced by the addition of a second metallic element to form a bimetallic cluster is selectivity. The selectivity of a catalyst is a measure of the extent to which the catalyst accelerates the reaction to form one or more of the desired products, which are usually intermediates, instead of undesired products which are often formed by reaction to the state of overall lowest free energy (4). Temperature, pressure, reactant composition, and extent of conversion as well as nature of the catalyst can all affect the selectivity. The selectivity is determined by the functionality of the catalyst and by thermodynamic equilibrium considerations. Thus it may be possible to avoid an undesired product by operating under conditions in which the equilibrium concentration of the product is negligible.

The selective hydrogenation of α, β unsaturated aldehydes to unsaturated alcohols is an important step in the synthesis of fine chemicals used in pharmaceuticals, perfumes and flavorings. For example, in the production of vitamin A all trans retinal is converted to retinol (5), or in other processes, citral is hydrogenated to citronellol (6) and furfural to furfuryl alcohol (7). While hydrogenation of the olefinic bond is readily achieved by most platinum group metal catalysts under mild reaction conditions (8), the selective hydrogenation of only the carbonyl group is considered by many researchers to be a difficult and challenging task when the carbonyl group is conjugated with the carbon-carbon double bond. Significant hydrogenation of the carbonyl group has been reported for the metals osmium and cobalt (9). Currently, there is no explanation available as to why for the hydrogenation of α, β unsaturated aldehydes heterogeneous catalytic reactions fail whereas homogeneous stoichiometric reductions (6,10) or homogeneous catalytic reactions appear to selectively produce the desired products. Much is still lacking in the fundamental understanding of the factors governing the selective heterogeneous catalytic reactions. In efforts to remedy the situation many investigators have begun to tackle this challenging task by studying the selective hydrogenation of simple molecules. This will undoubtedly have a tremendous impact on the future of specialty chemicals which will require selective intramolecular hydrogenation. For example, the selective hydrogenation of organic acids is currently difficult.

The objective of this research is to understand the effects of addition of a second metal such as Sn, Ag, and Cu to the Pt/SiO_2 system on the selectivity to crotyl alcohol in the hydrogenation of an α, β unsaturated aldehyde, crotonaldehyde. Crotonaldehyde and hydrogen react in a network of reactions:



The most desirable reaction is the formation of crotyl alcohol which is also the least thermodynamically favored. With pure metals and simple monofunctional molecules it has been established that hydrogenation of the C=C bond is always easier than that of the C=O bond. Hence, bimetallic Pt/SiO_2 catalysts have been used to modify this relation.

Both ^1H NMR (nuclear magnetic resonance) and microcalorimetry were used to characterize the Pt bimetallic systems and to determine the hydrogen adsorption states. ^1H NMR has the unique ability to obtain accurate dispersion measurements along with direct information about the existence of electronic interactions between the metals in the bimetallic catalyst system. Similarly, microcalorimetry is used to identify the existence of various hydrogen adsorption states and to characterize in detail the energetics of the hydrogen-metal-interaction.

Dissertation Organization

This dissertation contains two papers each presented in a form suitable for submission for publication in a technical journal along with general conclusions. The work reported in these two papers was carried out in collaboration with members of the same catalysis research group. The author of this dissertation will be the primary author of both of these manuscripts.

Literature Review

Selective Hydrogenation of α, β Unsaturated Aldehydes

An α, β unsaturated aldehyde is a multifunctional molecule which contains a carbonyl group directly conjugated to an olefinic group. Hydrogenation can occur at both places of unsaturation. Usually hydrogenation of the carbon-carbon double bond occurs more readily than hydrogenation of the carbonyl group, therefore the challenge lies in selectively hydrogenating the carbonyl group without simultaneous hydrogenation of the carbon-carbon double bond. Problems that are encountered when trying to selectively hydrogenate the α, β unsaturated aldehydes to the unsaturated alcohol include the following: 1) In hydrogenations carried out with unpromoted metals the reactivity of the unsubstituted isolated carbon-carbon double bond is always higher than the reactivity of the isolated carbonyl bond; 2) Thermodynamically it is always more favorable to produce a saturated aldehyde or saturated alcohol than an unsaturated aldehyde.

In 1925 Tuley and Adams (11) reported that the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol in ethanol could be achieved over platinum/platinum oxide upon addition of iron (II) chloride or by a combination of iron (II) chloride and zinc acetate in small amounts.

Rylander et al. (12,13) used the same catalyst combination of Tuley and Adams to investigate the selective hydrogenation of several α, β unsaturated aldehydes. They reproduced the results obtained by Tuley and Adams for the selective hydrogenation of cinnamaldehyde. Also, they found that the same catalyst system gave high yields of crotyl alcohol from crotonaldehyde. Rylander and coworkers noted that it was necessary to have both zinc and iron salts present simultaneously in order to selectively hydrogenate the carbonyl group. These metals are quite specific and many attempts were made to replace iron and/or zinc as a promoter. They discovered that silver could replace zinc but iron needed to be present with zinc or silver to give the desired unsaturated alcohol. Numerous experiments were tried with other metals palladium, ruthenium, and rhodium with or without metal modifiers such as iron, zinc, gold, silver, tin, calcium, copper, nickel, and lead, alone or in combination, but to no avail the saturated aldehyde was the only product.

Rylander et al. (12,13) also studied the effects of the solvent, the additives and the support used in the selective hydrogenation of α, β unsaturated aldehydes. The support can play an important role in determining the selectivity of the hydrogenation reaction. The unsaturated alcohol is the product when carbon and calcium carbonate are used for the supports but supports such as alumina and barium sulfate produce the saturated aldehyde. A correlation between the type of support, rate of reduction, and selectivity was not established. Lastly, they discovered that the selective hydrogenation of the carbonyl group in an α, β unsaturated aldehyde is difficult possibly due to the closeness of the functional groups and becomes easier if some substituents are present on the olefinic group.

Rylander and Steele (14) obtained high yields of allyl alcohol (73%), crotyl alcohol (90%) and cinnamyl alcohol (95%) in the selective hydrogenation of acrolein, crotonaldehyde and cinnamaldehyde, respectively with or without solvent present, but the system was reported to be erratic. The catalyst system used for this reaction was osmium supported on alumina or preferably on carbon. They reported that an increase in the temperature increased the rate of the reaction but at the expense of decreased selectivity.

Some of the research done in the 1970's concerning the selective hydrogenation of α, β unsaturated aldehydes includes the following. In 1970 Khidekel et al. (15) used a catalyst consisting of 5% iridium supported on carbon to selectively hydrogenate crotonaldehyde to crotyl alcohol with a yield of 90%. Steiner (16) used an unsupported platinum catalyst modified with cobalt to selectively hydrogenate β - methylcrotonaldehyde in n-butanol to the unsaturated alcohol. He obtained a yield of 91% of the unsaturated alcohol and found that the level of cobalt should be increased when dealing with more difficult selectivity problems. Ichikawa et al. (17) in 1977 used the same catalyst system of Tuley and Adams except that iron(II) sulfate was used instead of iron(II) chloride to study the selective hydrogenation of β - methylcrotonaldehyde. They obtained the unsaturated alcohol with a yield of 93%. Also, Ichikawa et al. (18) used platinum oxide modified with nickel and iron to reduce citral to citronellol with a yield of 96%. They noted that the unconjugated double bond remains whereas the conjugated double bond is reduced selectively. Ichikawa and Teizo (19) found that when iron was not present the yield of citronellol was only 83%. Lastly, Vanderspurt (20) used a supported rhenium catalyst to selectively hydrogenate acrolein to allyl alcohol in the vapor phase. Further studies of the system (21) lead to the result that the selectivity toward the unsaturated alcohol is dramatically increased (to ca. 60%) by addition of carbon monoxide or carbon disulfide to the process stream. The effect of carbon monoxide has been attributed to either a selective poisoning of the sites responsible for carbon-carbon double bond hydrogenation or to an electronic modification of the metal sites induced by the chemisorbed carbon monoxide.

In 1980 Jenck and Germain (22) studied the hydrogenations of aldehydes, ketones and olefins over copper chromite catalysts. They discovered the following order of reactivities in the competitive hydrogenations of these monofunctional compounds: carbonyl bond (aldehyde) > carbonyl bond (ketone) > carbon-carbon double bond (olefin). This scale was also reported to apply to nonconjugated bifunctional molecules (olefinic aldehydes and ketones). However, for conjugated compounds containing the C=C–C=O group, similar reaction rates for both double bonds and a lower enol selectivity were observed. The authors therefore suggest a 1,4 addition of hydrogen to the conjugated system.

Hubaut et al. (23,24) also examined the selective hydrogenation of α, β unsaturated aldehydes and ketones using copper chromite catalysts. The molecules investigated were crotonaldehyde, methacrolein and methyl vinyl ketone. In agreement with Jenck and Germain's results, they observed a lower reactivity of the carbonyl group in conjugated systems. They have shown that the selectivities in the hydrogenation of these compounds are controlled by the high polarization of these molecules and steric and electronic effects induced by the presence of a methyl substituent. The authors believe that the formation of the allylic alcohol corresponds to a 1,2 addition process and that the 1,4 addition process is responsible for the formation of the saturated aldehyde or ketone. The unsaturated alcohol, saturated aldehyde and the initial unsaturated aldehyde all compete for the same adsorption sites. They reported that the reaction becomes inhibited due to the strong adsorption of the allylic alcohols.

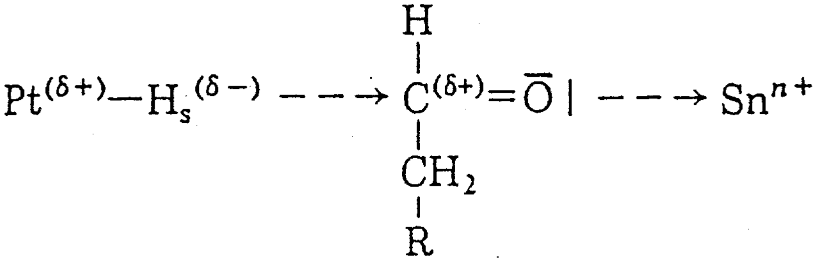
Sokolskii et al. (25) tried supporting palladium black on a variety of oxide systems for the hydrogenation of crotonaldehyde. These oxide systems included SiO_2, Al_2O_3, B_2O_3, MgO, Fe_2O_3, and ZnO. Regardless of the oxide additive, the reaction produced 100% butyraldehyde. However, Sokolskii et al. (26,27) reported a decrease in the reaction rate and an increase in the selectivity of the carbonyl group in the hydrogenation of α, β unsaturated aldehydes when certain oxides were added to ruthenium and osmium black.

Sokolskii et al. (28) have also studied the addition of iron(III) oxide to group VIII metals for the hydrogenation of crotonaldehyde in water at 293K. They reported that upon addition of iron(III) oxide the reaction rate decreased for osmium, ruthenium and platinum but increased for palladium, rhodium and iridium. The selectivity towards the carbonyl group increased over all of the group VIII metals with the exception of palladium which showed no hydrogenation of the carbonyl group upon addition of iron(III) oxide. The selectivity to the carbonyl group over the group VIII metals decreased in the following order Os > Pt > Ir > Ru > Rh. Addition of iron(III) oxide to platinum caused a drastic change in the direction of hydrogenation. The authors reported that over platinum black selectivity to the carbon-carbon double bond was 91% but in the presence of iron(III) oxide, hydrogenation of the carbonyl group occurred with a selectivity of 80%.

Galvagno and coworkers have studied extensively the selective hydrogenation of α, β unsaturated aldehydes in the liquid phase over platinum and ruthenium catalysts with and without promoters. Galvagno et al. (29,30) discovered that adding tin to platinum supported on nylon resulted in severe suppression of the hydrogenation of the carbon-carbon double bond and the carbon-carbon triple bond in propene and phenylacetylene, respectively. They proposed that the surface is enriched with tin which reduced the number of platinum active sites and/or that an electronic interaction exists between platinum and tin. Upon examination of the hydrogenation of hydrocinnamaldehyde, the saturated aldehyde formed when hydrogen is added to the carbon-carbon double bond of cinnamaldehyde, they observed that addition of minute amounts of tin increased the reaction rate drastically. A maximum in the reaction rate was reached at a tin content of 10% and subsequent additions in turn led to a decrease in the reaction rate.

In 1986 Galvagno and coworkers (31,32) also studied the selective hydrogenation of acrolein and cinnamaldehyde over platinum/nylon catalysts promoted with tin or germanium. They obtained selectivities of 65% allyl alcohol and 75% cinnamyl alcohol in the reductions of acrolein and cinnamaldehyde, respectively, over platinum-tin/nylon catalysts (31). When germanium was used in place of tin as a promoter a selectivity of 95% for cinnamyl alcohol was obtained (32). Other additives were investigated such as sodium, calcium, aluminum, cobalt, selenium and iron but only iron was found to be of any value as a promoter (33).

Galvagno and coworkers proposed that the addition of promoters has two main effects. One is to deactivate the platinum sites for the addition of hydrogen to the multiple carbon-carbon bond. This occurs by the presence of the additives blocking the active platinum sites or by an electronic interaction between the promoter and platinum which weakens the chemisorption bond between the substrate and the platinum site. Another effect is to activate the carbonyl group. The presence of the promoter increases the polarization charge of the carbonyl group which in turn enhances its reactivity toward chemisorbed hydrogen (see Figure 1).



$$\mathrm{Pt}^{(\delta+)}\text{—}\mathrm{H_s}^{(\delta-)} \dashrightarrow \underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{R}}}{\overset{\substack{\mathrm{H}\\ |}}{\mathrm{C}}}{}^{(\delta+)}=\overline{\mathrm{O}}\,| \dashrightarrow \mathrm{Sn}^{n+}$$

Figure 1. Selective activation of the carbonyl group by tin in the hydrogenation of α, β unsaturated aldehydes over PtSn catalysts (30)

Recently, Galvagno et al. (34-37) have been investigating the catalyst system of ruthenium supported on carbon for the selective hydrogenation of α, β unsaturated aldehydes. They concluded after thorough examination of the hydrogenations of cinnamaldehyde and citral in the liquid phase that the hydrogenations of α, β unsaturated aldehydes are structure insensitive (34,36). However, the selectivity of cinnamyl alcohol increased with ruthenium particle size but this was not the case for the unsaturated alcohols formed in the selective hydrogenation of citral. Therefore, the presence of steric constraints can modify the product distribution.

Galvagno and coworkers (35) have also been examining the addition of tin to the ruthenium/carbon catalyst system. After comparing the results obtained from the hydrogenations of β - methylstyrene and hydrocinnamaldehyde they suggested that tin behaves differently depending on the organic substrate. For example, the main effect of tin when there is a carbon-carbon double bond present is to block the surface ruthenium atoms and the effect of tin when there is a carbonyl group present is to activate this group which facilitates the transfer of hydrogen from adjacent sites.

In the selective hydrogenation of cinnamaldehyde over ruthenium-tin/carbon catalysts Galvagno et al. (37) obtained a 90% selectivity of cinnamyl alcohol with a tin content of approximately 30%. They suggested that tin is physically blocking the ruthenium metal sites and/or a ruthenium-tin alloy is forming which is responsible for the decrease in the number of surface ruthenium atoms as measured by carbon monoxide chemisorption. These sites are considered to be responsible for the carbon-carbon double bond hydrogenation. Another type of site available which is proposed to be created by the presence of tin ions is where the adsorption of cinnamaldehyde takes place through the carbonyl group. Hydrogen transfer from an adjacent Ru-H site occurs readily due to the polarization of the carbonyl group caused by tin.

Goupil et al. (38) investigated the use of metallic iron as a promoter for the platinum/carbon catalyst system. They concluded that the catalyst system consisted of platinum-iron bimetallic particles. They also reported that both the activity and selectivity to cinnamyl alcohol in the selective hydrogenation of cinnamaldehyde are greatly improved by the addition of metallic iron to the platinum/carbon catalyst. The initial selectivity of pure platinum supported on carbon was reported to be only 30% cinnamyl alcohol. Upon addition of 50 at.% iron a selectivity of 90% was achieved. The effect of metallic iron on the activity was found to be even more startling. The activity of a platinum/carbon catalyst containing 20 at.% iron was reported to be about 100 times greater than that of pure platinum.

Goupil (39) also discovered that in the hydrogenation of cinnamaldehyde selectivity to cinnamyl alcohol increased with increasing conversion of cinnamaldehyde. He has shown that addition of hydrocinnamaldehyde, the saturated aldehyde, to the reaction medium causes the cinnamaldehyde conversion to become inhibited. The saturated aldehyde produced in the reaction may remain adsorbed on the metal. The selectivity toward cinnamyl alcohol may then be altered either by a steric effect or by an electronic effect. In the case of the steric effect, cinnamaldehyde may be forced to adsorb end-on via the carbonyl group or in the case of the electronic effect, the adsorbed saturated aldehyde causes an increase in the charge density of the metal which would lower the probability for carbon-carbon double bond activation. In either case, an increase in the selectivity towards cinnamyl alcohol would result.

Giroir-Fendler, Richard and Gallezot (40-43) have been examining the hydrogenation of cinnamaldehyde and have found that different factors enhance the selectivity to cinnamyl alcohol. They have shown that platinum, ruthenium and rhodium catalysts supported with graphite as compared to catalysts supported with carbon have demonstrated an enhanced selectivity to cinnamyl alcohol (40,41). This has been attributed to a transfer in charge from the support to the metal which increases the charge density on platinum which in turn decreases the probability for the hydrogenation of the carbon-carbon double bond. Richard et al. (42) have also shown that the presence of iron atoms on the surface of platinum particles increases the likelihood of adsorption and activation of the carbonyl group. They suggest that the iron adatoms on the surface of the platinum particles carry a positive charge either due to incomplete reduction or because of an exchange of electrons from iron to platinum. Next the electron deficient iron adatoms can act as adsorption sites for the carbonyl groups of cinnamaldehyde molecules via donation of electrons from one of the unshared electron pairs of the oxygen atom. The scheme (42) is shown in Figure 2. They also reported a lower rate of hydrogenation of the carbon-carbon double bond in cinnamaldehyde with the platinum/carbon catalysts promoted with iron which also increases the selectivity to the unsaturated alcohol. It was suggested that this could be due to an increase in the charge density on platinum which decreases the probability of carbon-carbon double bond activation which involves a donation of π-electrons to the metal.

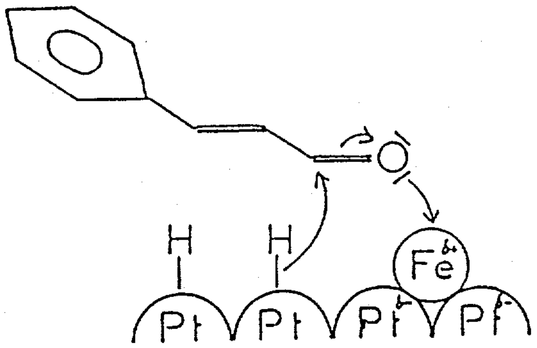


Figure 2. Scheme of the activation of the carbonyl group of the cinnamaldehyde molecule by iron atoms in Pt-Fe bimetallics (42)

Another way to increase the selectivity to the unsaturated alcohol is the use of shape-selective zeolites. Gallezot et al. (43) obtained very high selectivities of cinnamyl alcohol in the hydrogenation of cinnamaldehyde by using Y-type zeolites containing encaged metal particles. They found that hydrogenation of the carbonyl group is highly favored over hydrogenation of the carbon-carbon double bond due to the molecular constraints of the zeolite micropores. Because of the rigidity and dimension of the cinnamaldehyde molecule it can only adsorb end-on (via the carbonyl group).

Giroir-Fendler et al. (44) also found that geometric effects depending on the morphology of the metal particles and on the steric configuration of α, β unsaturated aldehyde molecules can modify the selectivity. It has been reported that large cobalt (45) or platinum (40) particles gave a higher selectivity to cinnamyl alcohol than smaller particles. Giroir-Fendler et al. (44) studied two rhodium supported on graphite catalysts. The composition, the pretreatment conditions and the reaction conditions were identical for the two catalysts. Both of the catalysts gave a low selectivity to cinnamyl alcohol which is no surprise since rhodium is highly active for the hydrogenation of carbon-carbon double bonds. However, one of the catalysts was much more selective than the other one which was attributed to the difference in particle morphology specifically the presence of 7 nm large faceted particles compared to 2-3 nm particles. Similar trends were found for platinum catalysts supported on graphite. The selectivities of the platinum catalyst supported on graphite were 91% and 98% at initial and 50% conversions of cinnamaldehyde, respectively. Such high selectivities are usually obtained only after promotion of platinum with metal salts (8,42) or on bimetallic catalysts (38,40). Giroir-Fendler et al. (44) also examined an alumina supported platinum catalyst and obtained selectivities of 74% and 76% at initial and 25% conversions of cinnamaldehyde, respectively in spite of the fact that alumina was found not to be a suitable support to obtain high selectivities of unsaturated alcohols in the selective hydrogenation of α, β unsaturated aldehydes (8).

Giroir-Fendler et al. (44) attribute all of the results reported above to the fact that metal particles exhibiting large faces as compared to the dimension of the cinnamaldehyde molecule are more selective than particles too small (< 2-3 nm) to present extended faces. They have suggested that on larger metal particles the aromatic ring, which is not bonded to the surface, lies at a distance exceeding 0.3 nm due to the presence of an energy barrier which prevents a closer approach. Under these conditions the cinnamaldehyde molecule is tilted and the carbonyl group is closer to the surface of the metal than the carbon-carbon double bond. Therefore, it is believed that on flat planes the carbonyl group is more easily activated hence, an increased selectivity to the unsaturated alcohol. In contrast there is no steric constraint for the approach and adsorption of either the carbon-carbon double bond or the carbonyl group on particles smaller than 2-3 nm due to the fact that the aromatic ring lies well above the surface of the metal as shown in the Figure 3.

Blackmond et al. (46,47) have also studied the selective hydrogenation of unsaturated aldehydes over zeolite-supported metals. In the liquid-phase selective hydrogenation of 3-methyl crotonaldehyde over ruthenium supported on NaY and KY zeolites both catalysts produced significant amounts of the saturated aldehyde. However, the K-exchanged catalyst demonstrated a threefold increase in the selectivity of the unsaturated alcohol compared to ruthenium/NaY. For platinum and rhodium catalysts supported on zeolites the same effect was demonstrated but to a lesser extent. They also studied this same reaction in the gas-phase and again the K-exchanged catalyst gave higher selectivities of the unsaturated alcohol compared to the Na-exchanged catalyst. Interestingly, the unsaturated alcohol was the major product for the Ru/KY catalyst which is in contrast with the liquid-phase results. It was suggested that the higher temperature used in the liquid-phase hydrogenation might account for the increased saturated aldehyde production through isomerization of the unsaturated alcohol. Simonik and Beranek (48) observed isomerization of crotyl alcohol to butyraldehyde in the selective hydrogenation of crotonaldehyde at 433K. They also reported that the isomerization of unsaturated alcohols to the corresponding

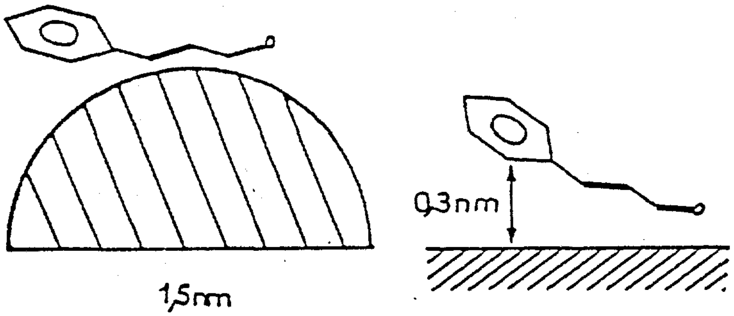


Figure 3. Scheme of cinnamaldehyde adsorption on a small metal particle and on a flat metal surface (44)

saturated aldehyde proceeds on metals such as copper, nickel and palladium and on oxides, especially aluminum oxide. Another possibility suggested to try and explain the increased production of the unsaturated alcohol in the gas phase compared to the liquid phase hydrogenation was the increased residence time of the products in the batch liquid-phase reaction as compared to the continuous flow gas-phase reaction. The products may not be in contact long enough in the gas-phase reaction to undergo secondary isomerization reactions.

Blackmond and coworkers have attributed the increase in selectivity towards the unsaturated alcohol in the hydrogenation of 3-methyl crotonaldehyde to an increase in the basicity of the support by exchanging K cations for Na cations in the Y zeolite. It is believed that a decrease in acidity results in an increased metal electron density which may cause a suppression in the carbon-carbon double bond hydrogenation rate combined with an increase in the carbonyl bond hydrogenation rate due to an interaction between the carbonyl group and the more basic zeolite cation.

A dual-site mechanism proposed by Richard et al. (42) for the hydrogenation of cinnamaldehyde over platinum-iron catalysts suggests that a cationic electron acceptor species such as iron preferentially activates the carbonyl group while reduced metal sites such as platinum provide the hydrogen for hydrogenation of the carbonyl bond. A mechanism similar to this is thought to be useful in explaining the increased unsaturated alcohol formation over ruthenium/KY. If the ruthenium particles are located within the zeolite supercages in close proximity to the potassium cations then a system exists with both metallic sites to provide hydrogen and cationic sites to activate the carbonyl group.

Blackmond et al. (47) have investigated geometric and electronic effects in the liquid-phase hydrogenation of cinnamaldehyde over zeolite supported metals such as ruthenium, platinum and rhodium. In the hydrogenation of cinnamaldehyde selectivity to cinnamyl alcohol was greatly increased when ruthenium was supported on either zeolite, KY or NaY, compared to ruthenium supported on carbon. Selectivity to cinnamyl alcohol also increased with increasing conversion of cinnamaldehyde, particularly for the zeolite-supported ruthenium. The results for platinum and rhodium supported on the two zeolites were reported to be similar to ruthenium. They found a small difference between the two types of zeolites for these two metals which indicates that the zeolite pore structure and not the electronic properties of the cation was the important fact in achieving a high cinnamyl alcohol selectivity. It is believed that the rigidity of the side chain of the cinnamaldehyde molecule and the bulkiness of the phenyl group hinders adsorption at the carbon-carbon double bond in the zeolite pores.

Further studies on the effects of support and alkali promoters in the gas-phase hydrogenation of 3-methyl crotonaldehyde have recently been tackled by Blackmond et al. (49-52). They reported that unsupported ruthenium and ruthenium/SiO_2 catalysts produced approximately 100% saturated aldehyde. The selectivity towards the unsaturated alcohol was increased in the following order Ru/NaY < Ru/KY < Ru/CsY when modified Y zeolites were used as supports. Addition of potassium as a promoter to the ruthenium supported on silica catalyst caused a dramatic increase in the selectivity of the unsaturated alcohol to over 70%. It was also noted that the activation energy for formation of the saturated aldehyde was similar for the promoted and unpromoted catalysts but the rate for this reaction was significantly suppressed for the promoted catalyst. They have suggested that the alkali species added to the ruthenium/SiO_2 catalyst had a dual effect of suppressing the hydrogenation at the carbon-carbon double bond and enhancing the hydrogenation at the carbonyl function by altering adsorption of the 3-methyl crotonaldehyde molecule to polarize the carbonyl bond which would increase selectivity to the unsaturated alcohol. IR evidence was produced to support their suggestion that potassium cations help to polarize the carbonyl group of the molecule.

It was suggested by Waghray et al. (50) that potassium also blocks the low coordination ruthenium sites which exhibit higher activity for the hydrogenation of the carbon-carbon double bond than the high coordination sites. Nitta et al. (45) have examined the structure sensitivity of these selective hydrogenation reactions and have shown that smaller cobalt particles demonstrated higher selectivity towards the saturated aldehyde than did larger particles. It is can be assumed that the small cobalt particles used in the above study contained a larger amount of low coordination metal sites than did the larger ones (53) therefore, supporting the above proposal that the low coordination sites are active for carbon-carbon double bond hydrogenation.

In order to clarify the role of an alkali species in the selective hydrogenation of 3-methyl crotonaldehyde Blackmond and Waghray (51) concentrated on various catalyst preparations to give them some clues. They reported that the overall rate of reaction was relatively unaffected by the presence of potassium due to the fact that an increase in the rate of formation of the unsaturated alcohol was compensated by a decrease in the rate of formation of the saturated aldehyde. They proposed the model shown in Figure 4 to explain the above behavior. The alkali species interacts with the ruthenium to create sites at the Ru-K interface which are active for unsaturated alcohol formation and it can also block ruthenium sites active for saturated aldehyde formation.

Addition of potassium also suppressed the extensive adsorption of 3-methyl crotonaldehyde on the support. Therefore, they believed that both the interaction of potassium with the support and with ruthenium influenced the catalytic behavior of ruthenium. They also demonstrated that the degree of closeness of the promoter to the catalytically active ruthenium sites is an important parameter in determining product selectivity.

Waghray and Blackmond (52) incorporated *in situ* infrared spectroscopy

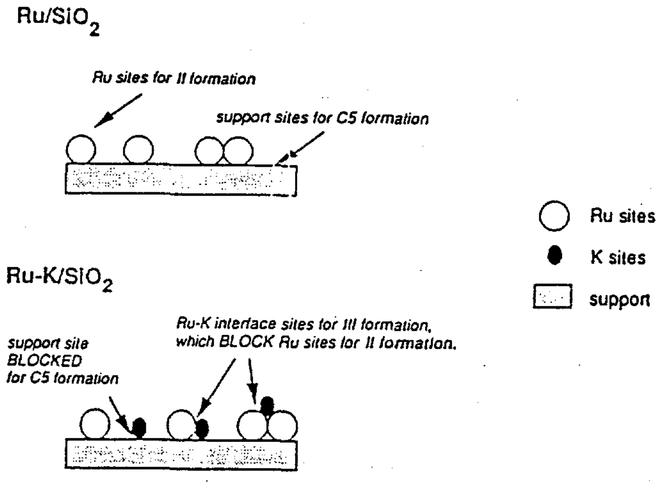


Figure 4. Schematic of proposed active sites for hydrogenation products on standard unpromoted and potassium-promoted Ru/SiO_2 catalysts. II represents the saturated aldehyde and III represents the unsaturated alcohol (51)

along with flow reaction studies of the hydrogenation of 3-methyl crotonaldehyde over ruthenium/SiO_2 and potassium promoted ruthenium/SiO_2 to concentrate on the changes observed during the initial period of the reaction leading to steady state operation. They observed significant changes in the reaction rate and product selectivities during the initial stages of the reaction before steady state operation was achieved. It was suggested that the composition of species on the catalyst surface during this initial period underwent many alterations. This is very important in the case of the ruthenium/SiO_2 catalyst promoted with potassium due to the increase in selectivity of the unsaturated alcohol from 10% to approximately 80% at steady state. Therefore, it is implied that a surface covered with a variety of adsorbed reactants, products and organic fragments that developed over a period of time is responsible for the increased selectivity towards the unsaturated alcohol not the clean catalyst surface.

Infrared evidence led them to believe that a significant fraction of the adsorption of 3-methyl crotonaldehyde occurred through hydrogen bonding between the carbonyl function and the hydroxyl groups on the silica. Also, hydrogenation of the carbon-carbon double bond of 3-methyl crotonaldehyde to produce the saturated aldehyde followed by partial decarbonylation to form isobutane and adsorbed carbon monoxide took place on the ruthenium metal in a process referred to as "reverse migratory insertion". The carbon-carbon double bond hydrogenation and aldehyde decarbonylation reactions were affected by the presence of potassium . It was suggested that the promoter may act to inhibit both the carbon-carbon double bond hydrogenation and decarbonylation reaction. However, IR was not of any help in determining how the promoter enhanced the rate of formation of the unsaturated alcohol.

Vannice and coworkers (54-56) have also been intensively studying the effects of supports on the intramolecular selectivity of crotonaldehyde hydrogenation over platinum. They discovered that certain supports such as TiO_2 can drastically increase the rate of carbon monoxide hydrogenation over Group VIII metals. However, this rate increase has not been observed for the hydrogenation of carbon-carbon double bonds or aromatic rings. This led to the possibility that maybe the metal-support effect responsible for activation of the carbon monoxide molecule might be utilized to activate the carbonyl function in α, β unsaturated aldehydes rather than the olefinic bond. They proposed that special sites are created at the metal-support interface. The site is composed of at least one metal atom adjacent to a defect site on the support such as a Ti^{3+} cation or an oxygen vacancy. Interaction occurs between the oxygen atom of the carbonyl group and the support (see Figure 5). Reduction at a high temperature causes these TiO_x species to migrate over the surface thereby creating more Pt-TiO_x sites to activate the carbonyl bond of the α, β unsaturated aldehyde.

For the hydrogenation of crotonaldehyde over platinum supported on SiO_2 and Al_2O_3 Vannice and Sen (54) obtained 100% butyraldehyde. The same reaction over a platinum/TiO_2 catalyst reduced at 473K produced crotyl alcohol with a selectivity of 14%. Over a platinum/TiO_2 catalyst reduced at 773K a selectivity of 37% crotyl alcohol was achieved. Activities (per gram platinum) reported did not vary significantly over the different supported catalysts but the turnover frequency values for the catalyst reduced at 773K were markedly higher. Another important result discovered was that the isomerization of crotyl alcohol to butyraldehyde in the presence of hydrogen is nearly three times faster on platinum supported on silica than on platinum supported on either titania or alumina. Therefore, these results verify that the Metal Support Interaction (MSI) effect proposed by Vannice and coworkers can be used to improve catalysts for the selective hydrogenation of carbonyl functions in multifunctional molecules.

Yoshitake et al. (57, 58) have examined iridium, platinum and rhodium supported on niobia catalysts in the hydrogenation of acrolein. They discovered that the selectivity towards the carbonyl group was enhanced upon HTR (high temperature reduction). They attributed this increase in selectivity to the formation of new catalytic sites on the periphery of the metal particles due to migration of the NbO_x islands onto the metal particles. They have proposed that two sites exist on the HTR catalysts. One site, the bare metal surface, is where hydrogen dissociation occurs and the other site, the periphery of NbO_x islands, is

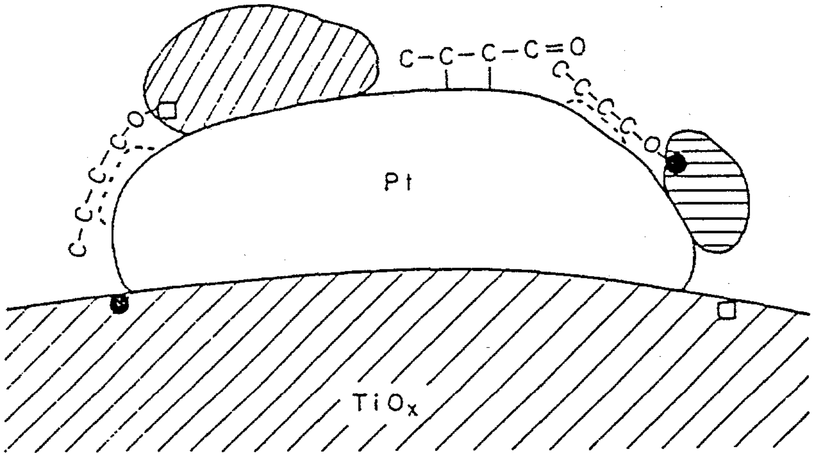


Figure 5. Interfacial site model for activation of carbonyl bonds in Pt/TiO_2 catalysts using crotonaldehyde as example: (•) Ti^{3+} cation; (□) oxygen vacancy (56)

where adsorbed acrolein and hydrogen atoms react. Both propanal and allyl alcohol are formed through η^4 (C–C–C–O) intermediates on the peripheral sites of NbO_x islands. The differences in the catalytic behavior among the SMSI (strong metal support interaction) metal catalysts is reported to be due to electronic effects. The SMSI effects were larger with iridium supported on niobia than with rhodium on niobia. They reported that rhodium was apparently not electronically modified. Platinum and iridium were thought to be modified due to an observed difference in the activation energies between the low temperature reduction and high temperature reduction catalysts.

Wismeijer et al. (59, 60) have also studied the effects of supports in the hydrogenation of crotonaldehyde and citronellal over ruthenium supported on titania. They reported that in the hydrogenation of crotonaldehyde ruthenium supported on titania had greater activity and selectivity for the carbonyl bond compared to the olefinic bond than did ruthenium supported on silica. No selectivities for crotyl alcohol were given. For citronellal hydrogenation the titania supported ruthenium catalyst was once again more active and selective than the silica supported catalyst when activated at a temperature of 773K. However, the ruthenium supported on silica catalyst became more selective above 773K but at the expense of the activity.

Kaspar et al. (61) have examined the influence of high temperature on the activity and selectivity in the hydrogenation of crotonaldehyde over groups VIII and VIIII metal catalysts supported on titania. They found that the positive effects of HTR (773K for 3 hours) on the formation of the unsaturated alcohol depends strongly on the nature of the metal as well as the nature of the organic reactant. Low dispersion ruthenium and iridium catalysts demonstrated an increase in selectivity towards crotyl alcohol upon HTR treatment while a decrease in activity was reported for rhodium and osmium catalysts. The authors have suggested that HTR induces the decoration of the metal particles by titania sub-oxides which produces new catalytic sites selective for unsaturated alcohol formation. The results obtained support the ideas of other researchers (54-56).

Touroude (62) found that in the hydrogenation of acrolein monometallic platinum and osmium supported on alumina catalysts were effective for hydrogenation of the carbonyl bond. Touroude et al. (63) have also studied the effects of variations in the partial pressure of crotonaldehyde on the activity and selectivity in the hydrogenation of crotonaldehyde over platinum supported on titania. They reported that the total activity of the catalyst, either at the initial stages of the reaction or at steady state, was independent of crotonaldehyde pressure therefore, the authors suggested that the surface of the catalyst was completely covered by crotonaldehyde. They also found that at the initial stage of the reaction the hydrogenation of crotonaldehyde to butyraldehyde was largely poisoned as well as the consecutive hydrogenation of crotyl alcohol to butanol. However, the hydrogenation of crotonaldehyde was not affected. Hence, the authors believe that the transient period corresponds to selective poisoning of the carbon-carbon double bond sites while the carbonyl sites are not poisoned.

Touroude and coworkers have suggested that their results provide evidence of the existence of two types of sites, one for hydrogenation of the olefinic bond and one for hydrogenation of the carbonyl bond. They believe that the hydrogenation of the olefinic bond takes place on the metallic sites which are poisoned in the initial stages of the reaction. The hydrogenation of the carbonyl bond occurs at the interfacial sites between the support and the metal particles which has already been proposed for titania supported catalysts (54-56,59,60). However, the catalysts used in this study were only reduced at 200°C which is in contrast to the SMSI state reported by other researchers. The authors have proposed the existence of other interfacial sites which are reactive for carbonyl group hydrogenation and sensitive to hydrogen pressure since the authors observed an increase in the yield of crotyl alcohol with an increase of the ratio $P_{H2} / P_{crotonaldehyde}$.

Raab and Lercher (64-67) investigated the effects of addition of a second metal to supported platinum catalysts and the use of partially reducible supports such as titania in the selective hydrogenation of crotonaldehyde. Raab and Lercher modified the catalytic properties of platinum in comparison to platinum supported on silica by addition of three non noble metal promoters (nickel, tin and gallium) and the support titania. The bimetallic platinum-gallium/SiO_2 catalyst demonstrated the highest selectivity to crotyl alcohol with a value of 56% followed by platinum/TiO_2 (46%), platinum-tin/SiO_2 (31%) and platinum-nickel/SiO_2 (2%). The platinum supported on silica catalyst produced 100% butyraldehyde. They have shown that enhancement of the selectivity towards hydrogenation of the carbonyl bond is affiliated with the presence of polarity at the metal surface. They suggest that the polarity at the surface may originate from addition of a second metal to platinum which may cause e.g., a charge transfer to occur when the electronegativities of the two metals in the alloy are drastically different from each other. Polarity may also originate from metal ions or metal oxide particles decorating the surface of the platinum crystallites acting as strong electron pair acceptor sites for the free electron pairs of the oxygen atom of the carbonyl group.

Raab and Lercher have shown that for platinum-nickel/SiO_2 catalysts an increase in the rate of the selective hydrogenation of the carbonyl bond is proportional to the concentration of the PtNi phase which passes through a maximum with a catalyst containing 50 at.% nickel. Evidence that nickel has a slightly positive charge in the PtNi phase has been obtained from Xanes measurements (68). They believe that the positive charge of the nickel atoms might increase interaction of the carbonyl group with the catalyst surface. This increased interaction may also increase polarization of the carbonyl bond and enhance hydrogenation of the carbonyl group. The increase in the rate of carbon-carbon double bond hydrogenation is also proportional to the presence of nickel. The nickel/SiO_2 catalyst was the most active for this reaction. The increase in the hydrogenation rate of the carbon-carbon double bond overcompensates the positive effects of nickel in the hydrogenation of the carbonyl group. The platinum-nickel bimetallic phase is proposed to be active for carbonyl group hydrogenation and a pure nickel or platinum surface is responsible for hydrogenation of the carbon-carbon double bond.

Raab and Lercher suggested that the situation demonstrated by the platinum-nickel/SiO_2 catalyst is similar for the platinum-tin/SiO_2 catalyst. The significantly higher rate of hydrogenation of the carbonyl group for the platinum-tin/SiO_2 catalyst compared to the bimetallic platinum-nickel catalyst was suggested to be due to the increased activity of the platinum-tin bimetallic sites. They believe that tin has a larger positive charge than nickel. Also noted was the fact that the deactivation as a function of time on stream for the two catalysts was very similar. The rate of hydrogenation of crotonaldehyde to crotyl alcohol decreases significantly faster with the number of turnovers (TON = molecules converted/accessible metal atom) than the rate of hydrogenation of crotonaldehyde to butyraldehyde.

For the Pt/TiO_2 catalyst the Ti^{x+} cations were proposed to be the electron pair acceptor sites necessary to enhance the hydrogenation rate of the carbonyl group. Raab and Lercher suggest that the electron pair acceptor strength is higher for the Ti^{x+} cation than for the tin or nickel cations which would possibly create a stronger interaction between the cation and the carbonyl group. This would explain the higher selectivity to crotyl alcohol reported on Pt/TiO_2 compared to Pt-Ni/SiO_2 and Pt-Sn/SiO_2. They also believe that since gallium is very difficult to reduce that part of it is present in the non reduced form which would result in positively charged gallium oxide species which are similar to titanium oxides. The rate of hydrogenation to crotyl alcohol and butyraldehyde both decreased in parallel over these two catalysts which is strikingly different to the results reported on Pt-Ni and Pt-Sn supported on silica. No reason for the differences in deactivation were given.

Marinelli et al. (69-70) studied the hydrogenation of acrolein over various modified platinum catalysts. They examined the influences of alloying, poisoning and promoting of silica-supported platinum catalysts in the selective hydrogenation of acrolein to allyl alcohol. A nickel catalyst and a nickel-copper catalyst both supported on silica mainly produced the saturated aldehyde, propanal. Therefore, alloying nickel with copper does not affect the selectivity of the catalyst towards the unsaturated alcohol. The same effect is observed when the bimetallic catalyst platinum-copper/SiO_2 is used for the reaction. A slight enhancement of 2-3% in selectivity towards allyl alcohol is achieved when comparing the platinum/SiO_2 catalyst and the bimetallic platinum-copper/SiO_2 catalyst.

Marinelli and coworkers also studied the effects of addition of sulfur and carbon monoxide in the hydrogenation of acrolein. Three effects are expected to occur upon addition of carbon monoxide to the reaction. Carbon monoxide displaces hydrogen from the metallic surface so the rate of hydrogenation is expected to decrease drastically (71). It also displaces weakly bound olefins (π-complexed or di-σ-complexed) which should produce an added suppression of adsorption through the carbon-carbon double bond (72). The last effect being the displacement of molecules bound through the carbonyl bond to the metal or promoter surface. The first two effects would decrease the rate of hydrogenation of the olefinic bond and the last effect would decrease the rate of hydrogenation of the carbonyl group.

To examine the effect of presulfurization two series of platinum and copper catalysts were prepared one was supported on silica and the other on alumina. Different degrees and methods of adding thiophene to the catalysts were used. They reported that none of the four catalysts studied demonstrated any substantial increase in the selectivity to allyl alcohol. The selectivity did not even exceed 8% for any of the presulfided catalysts. These results disagree with results produced by Hutchings et al. (73) where a selectivity of 46% to allyl alcohol was obtained using a sulfided copper supported on alumina catalyst in the hydrogenation of acrolein. Hutchings and coworkers also used the same catalyst system in the hydrogenation of crotonaldehyde to obtain a selectivity of 64% crotyl alcohol compared to a selectivity of less than 10% on an unsulfided alumina supported catalyst. They attributed this enhanced selectivity to crotyl alcohol to the presence of sulfur in the form of thiophene which is thought to selectively poison the hydrogenation of the carbon-carbon double bond instead of the carbonyl bond.

Differences in the selectivity behavior of platinum supported on silica catalysts promoted by transition metal oxides and non-transition metal oxides were studied by Marinelli et al. (69) by adding carbon monoxide pulses during the hydrogenation reaction. Pt-Sn/SiO_2 and Pt-V/SiO_2 were the two catalysts used in the study. Pulses of carbon monoxide lead to a reversible suppression of all products for both the catalysts. Interestingly, the degree of suppression is not the same for all products. In both cases carbon monoxide strongly suppresses propanal formation. The difference between the two catalysts is in the formation of the unsaturated (allyl) and saturated (1-propanol) alcohols. Over the Pt-Sn catalyst carbon monoxide has a temporary positive effect on the selectivity to allyl alcohol but over the Pt-V catalyst selectivity to allyl alcohol and 1-propanol are both increased. The authors believe that since the selectivity towards the saturated alcohol is increased that a large part of the alcohol must be produced by a consecutive reaction of allyl alcohol to 1-propanol. The results over the bimetallic Pt-V catalyst are not surprising because various transition metal oxides are good promoters for the hydrogenation of aldehydes to alcohols in the production of higher alcohols from synthesis gas (74).

Marinelli et al. (69) also studied the consequences of addition of various metal oxides as promoters to a series of silica supported platinum catalysts in the hydrogenation of acrolein. The dominant product found for all of the catalysts was propanal. Sodium and potassium demonstrated no positive effect of the selectivity to allyl alcohol. Various transition metals were used as promoters and a slight increase of approximately 2-7% in selectivity to allyl alcohol which is dependent on the chosen promoter was reported. A drastic improvement in selectivity was achieved only when non-transition elements such as gallium, germaniun and tin were used as promoters. Selectivities to allyl alcohol were 17%, 9% and 25%, respectively. Therefore, the strongest promoting effect was due to the presence of tin. Various amounts of tin were added to the platinum supported on silica catalyst and a maximum in selectivity to allyl alcohol was reported with tin contents of around 20-25%.

The rates of formation of propanal, allyl alcohol and 1-propanol were also reported. In general, the presence of a promoter increased the rate of hydrogenation of the carbon-carbon double bond as well as the rate of hydrogenation of the carbonyl bond. The addition of a transition metal promoter e.g., iron to Pt/SiO_2 increased the reactivity of the carbonyl group but this only resulted in a slight improvement in the selectivity to allyl alcohol which is due to the fact that it also increases the rate of formation of propanal. When tin was used as a promoter the rate of hydrogenation of the carbonyl bond was enhanced by a factor of 50 to 100 compared to the rate of hydrogenation of the carbon-carbon double bond which was enhanced only by a factor of about 3 to 4.5.

When active atoms were diluted with less active atoms there was no significant increase in selectivity to allyl alcohol therefore, Marinelli and coworkers believe that the effect of ensemble size is of minor importance. They have also shown that addition of certain promoters can have a positive effect on the selectivity towards allyl alcohol. They expressed great interest in the fact that transition metal oxides were not better promoters in the selective hydrogenation of acrolein. They suggested that a possible reason for this behavior could be that transition metal promoters adsorb hydrogen and/or form chemisorption bonds with the olefinic group. The fact that the rate of propanal formation increased with addition of transition metal promoters supports the idea. Also, the results from the carbon monoxide pulse experiments on Pt-Sn/SiO_2 and Pt-V/SiO_2 where the selectivity to 1-propanol was only enhanced on the catalyst promoted by the transition metal because of the affinity of vanadium for the carbon-carbon double bond provides additional support.

Marinelli and coworkers believe that a better understanding of how the modes of adsorption of the olefinic group compared to the carbonyl group affect the selectivity and activity of the α, β unsaturated aldehydes could be achieved by studying the influence of substitution at either the carbon-carbon double bond or the carbonyl bond. The hydrogenation reactions with two series of methyl-substituted aliphatic α, β unsaturated aldehydes took place over various promoted platinum supported on silica catalysts. The metals used as promoters included the following: sodium, vanadium, titanium, iron, gallium, germanium and tin. The first series of aldehydes contained acrolein, crotonaldehyde and 3-methyl crotonaldehyde. Crotonaldehyde is formed by substitution on the terminal olefinic carbon atom of acrolein with one methyl group and 3-methyl crotonaldehyde is formed by substitution with two methyl groups on the terminal olefinic carbon atom. In order to study the effect of a methyl substituent on the olefinic group with one on the carbonyl group, the second group of organic compounds contained acrolein which was substituted either on the internal olefinic carbon atom to give methacrolein or on the carboxylic atom to form methyl vinyl ketone.

For acrolein, crotonaldehyde and 3-methyl crotonaldehyde an enhanced selectivity towards the unsaturated alcohol was reported for all the unpromoted and promoted platinum catalysts supported on silica with increasing substitution on the terminal olefinic carbon atom. The selectivity to allyl alcohol achieved in the hydrogenation of acrolein over the Pt-Fe/SiO_2 catalyst was about 7%. When crotonaldehyde and 3-methyl crotonaldehyde were hydrogenated over the same catalyst selectivities to the corresponding unsaturated alcohol were 28% and 80%, respectively. The authors believe that the ability of iron cations to activate both the hydrogenation of the carbon-carbon double bond and the carbonyl group might account for the low selectivity to allyl alcohol in the hydrogenation of an unsubstituted α, β unsaturated aldehyde such as acrolein. However, when iron is used as a promoter a dramatic increase in the activity and selectivity in the formation of the unsaturated alcohol is demonstrated with increasing methyl substitution at the olefinic group which causes it to become sterically hindered.

The selectivity to the unsaturated alcohol was found to be nearly the same for acrolein and methacrolein over the unpromoted and sodium, iron, gallium and tin promoted platinum catalysts. Over titanium and vanadium promoted catalysts an increase in selectivity by a factor of two towards the unsaturated alcohol for methacrolein hydrogenation versus acrolein hydrogenation was reported. An increase in selectivity by a factor of six was obtained with the Pt-Ge/SiO_2 catalyst. The selectivity to the saturated aldehyde was found to be higher in the hydrogenation of acrolein compared to methacrolein hydrogenation. The authors believe that the olefinic group is slightly stabilized by the presence of the methyl substituent.

When the hydrogenation of the methyl vinyl ketone was compared to the hydrogenation of acrolein a substantial decrease in the selectivity to the unsaturated alcohol was observed. Another surprising finding was that the activity to the saturated aldehyde was quite high in the hydrogenation of methyl vinyl ketone. The deactivation for the course of the experiment was reported to be negligible for methyl vinyl ketone but in the hydrogenation of the α, β unsaturated aldehydes there was a considerable amount of deactivation in the first hour.

Whenever the carbon-carbon double bond is sterically hindered the reactivity of this group is always decreased no matter what substitution is present. Beccat et al. (75) have shown that the selectivity to unsaturated alcohols when the olefinic group was sterically screened by the presence of methyl groups is significant even when pure metals are used. Crotonaldehyde and cinnamaldehyde have shown to be selectively hydrogenated by a large variety of oxides as promoters (26, 27, 31, 33, 37, 64, 65, 67, 69, 70, 76, 80), even iron containing compounds (11-13, 28, 33, 38, 42, 48, 69, 70, 75, 80). Only the non-transition metal oxides have proved to be successful promoters in the selective hydrogenation of acrolein. Therefore, Marinelli et al. (69) have suggested that the ratio in which the promoter activates the carbon-carbon double bond and the carbonyl bond is influenced by the accessibility of the olefinic bond as well as the nature of the promoting cation.

Noller and Lin (76) obtained a selectivity of 54% for crotyl alcohol in the hydrogenation of crotonaldehyde over 21% NiO - 10%CuO/Al_2O_3. Both metal oxides had to be present for any formation of crotyl alcohol.

Nitta et al. (77) used cobalt catalysts supported on silica prepared by a precipitation method from cobalt chloride to obtain both high activities and selectivities in the hydrogenation of crotonaldehyde and cinnamaldehyde to the corresponding unsaturated alcohol. Selectivities of 84% and 96% respectively at conversions of 50-90% were reported. Nitta and coworkers examined various starting salts in the preparation of the silica supported cobalt catalyst but the chloride precursor exhibited the highest selectivity to the unsaturated alcohol regardless of the support used. They have attributed this enhanced selectivity to the presence of chlorine which gives a favorable crystalline size distribution of cobalt during hydrogen reduction by facilitating the reduction of cobalt species with metal-support interaction. The authors also suggest that chlorine remaining on the surface of the catalyst after hydrogen reduction hampers the carbon-carbon double bond activation which would also lead to an enhanced unsaturated alcohol selectivity. The reverse effect has been observed over platinum and ruthenium catalysts by Vannice and Wismeijer.

Coq et al. (78) have recently been studying the selective hydrogenation of acrolein over group VIII metal catalysts. Various supports such as alumina, silica, titania, graphite and zirconia were investigated. Cobalt, nickel and ruthenium catalysts gave the highest initial selectivity to allyl alcohol regardless of the support used. Platinum catalysts demonstrated the highest specific activity but were not as selective to allyl alcohol as the other metal catalysts. The ruthenium catalysts supported on zirconia gave the highest selectivity to allyl alcohol which was suggested to be possibly due to alloying between ruthenium and zirconium. The authors also reported that smaller ruthenium particles are the least selective in the formation of allyl alcohol. The selectivity to allyl alcohol was initially quite high but decreased quickly with time. Selectivity to acetone and propanal were reported to increase monotonically with time. The authors believe that this may be due to the presence of different sites for the formation of allyl alcohol and propanal with the site involved in the formation of allyl alcohol deactivating rapidly.

Interestingly, Coq and coworkers reported a high selectivity to acetone which has not yet been reported as a product for the hydrogenation of acrolein. The authors noted that changing the ruthenium particle size did not significantly modify the selectivity to acetone, however the nature of the support had a strong influence on the formation of acetone. When supported on zirconia and graphite the ruthenium catalysts suppressed acetone formation. The authors speculated that acetone is formed through a 1,4 diadsorbed intermediate on an electron-deficient site which might be situated at the interface between the support and the metal particles.

Coq and coworkers obtained a higher selectivity to allyl alcohol on ruthenium supported on silica than on ruthenium catalysts supported on titania reduced at 773K. This is in contrast with results (54-56,59,60) reported that the support silica was not as selective as titania in the hydrogenation of crotonaldehyde. The authors gave no explanation for the increased selectivity observed on ruthenium/SiO_2 but didn't rule out the possibility of impurities.

Coq et al. (79) also investigated the selective hydrogenation of substituted acrolein over bimetallic ruthenium catalysts. The bimetallic catalysts were formed by using the controlled surface reaction method. They examined the addition of Sn, Fe, Ge, Sb and Zn to Ru/Al_2O_3 catalysts. A sharp decrease in the hydrogen uptake was reported over the bimetallic catalysts which is clearly related to the presence of the second metal at the surface of the bimetallic particles. The hydrogenation of acrolein was carried out at 353K. Addition of the second metal promoted the activity and the TOF (number of reactant molecules transported per hour per surface Ru atom) was increased by a factor of approximately 5-9 depending on the promoter. The selectivity to allyl alcohol was increased only on Ru-Sn/Al_2O_3. On Ru-Ge and Ru-Zn supported on alumina the selectivity to the saturated aldehyde, propanal, was increased dramatically.

With increasing substitution of the carbon-carbon double bond of acrolein the selectivity to the unsaturated alcohol increased drastically. Coq and coworkers suggested that the key factor in determining the selectivity to the unsaturated alcohol in α, β unsaturated aldehyde hydrogenations is the tilting of the alkyl chain far from the surface. They claim that this factor is more important than activation of the carbonyl bond by electron deficient species. Tin is the only modifier out of Sn, Fe, Zn, Ge and Sb to depress the chemisorption strength between the carbon-carbon double bond and the ruthenium surface.

Lastly, Coq et al. (80) investigated the liquid phase hydrogenation of cinnamaldehyde over supported ruthenium catalysts to examine the effects of particle size, bimetallics and nature of the support. The TOF increased by a factor of 10-15 from small to large ruthenium particles. This behavior was not demonstrated on Ru/C catalysts of different dispersions. The selectivity to cinnamyl alcohol increased from 22% on 1 nm Ru particles to 80% on large crystallites of bulk Ru which agrees with the results of Galvagno et al. (33). However, in their earlier study on the hydrogenation of acrolein the selectivity to allyl alcohol did not change much with Ru particle size. The TOF was increased by a factor of 2-6 upon addition of the second metal. Over the bimetallic catalysts they obtained high values of initial selectivity compared to Ru/Al_2O_3. These values were not sustained at higher cinnamaldehyde conversions. Therefore, they suggested that the addition of the second metal to ruthenium has the same effect on initial selectivity as the catalyst which has the saturated aldehyde, hydrocinnamaldehyde, adsorbed on the surface. Chemisorbed hydrocinnamaldehyde hinders the adsorption of cinnamaldehyde which forces the molecule to adsorb via the carbonyl group. They believe that the main effect of addition of the modifier appears to be due to the dilution of the Ru surface atoms by the inactive second metal which would make the activation of the carbon-carbon double bond more difficult. However, a electronic effect was suggested for the Ru-Sn/Al_2O_3 catalyst due to an increased selectivity to cinnamyl alcohol at higher conversions of cinnamaldehyde.

The selectivity to cinnamyl alcohol is only dependent on ruthenium particle size and not the nature of the support when supported on alumina, silica or graphite. A good cinnamyl alcohol selectivity and a high TOF were obtained on a Ru/TiO_2 catalyst. An increase in activity and selectivity for the hydrogenation of the carbonyl bond was previously observed for acrolein and crotonaldehyde which was attributed to the polarization of the carbonyl bond by the migrating TiO_x species. The Ru/ZrO_2 catalyst behaved similarly to the Ru/TiO_2 catalyst. Zirconia was found to be the most effective support in terms of selectivity to cinnamyl alcohol. Ruthenium supported on amorphous zirconia gave the highest selectivity to cinnamyl alcohol. The increase in the selectivity to cinnamyl alcohol over the Ru/ZrO_2 catalyst was suggested to be due to interfacial Ru-Zr^{n+} sites at the periphery of the particles (81). On the Ru/ZrO_2 catalysts the presence of these sites decreases the strength of the carbonyl bond making it more susceptible to an attack by hydrogen.

Listed in Table 1 is a summary of the researchers, reactants, products, catalysts and reaction conditions used in the selective hydrogenation of α, β unsaturated aldehydes. Table 2 provides the reader with structural examples of the most commonly studied α, β unsaturated aldehydes and the products formed upon hydrogenation. Table 3 lists a summary of the catalytic effects proposed by researchers for increased selectivity to the unsaturated alcohol in the selective hydrogenation of α, β unsaturated aldehydes.

TABLE 1. Summary of literature review of the selective hydrogenation of α, β unsaturated aldehydes

RESEARCHER	REACTANT	PRODUCT	CATALYST	CONDITIONS
Tuley and Adams (11) Rylander et al. (12)	cinnamaldehyde	cinnamyl alcohol	Pt black & PtO_2 with $FeCl_2$ and/or $Zn(OAc)_2$	ethanol hexane
Rylander et al. (12)	crotonaldehyde	crotyl alcohol	Pt/PtO_2 with $FeCl_2$ and $Zn(OAc)_2$; or $FeCl_2$ and $AgNO_3$	ethanol
Rylander et al. (12,13)	cinnamaldehyde crotonaldehyde	90% cinnamyl alcohol 89% crotyl alcohol (carbon as support)	Pt/C or $CaCO_3$ with $FeCl_2$ and $Zn(OAc)_2$; or $FeCl_2$ and $AgNO_3$	hexane ethanol T = 298K; P = 50 psig
Rylander et al. (12)	crotonaldehyde	butyraldehyde	Pt/Al_2O_3 or $BaSO_4$ with $FeCl_2$ and $Zn(OAc)_2$; or $FeCl_2$ and $AgNO_3$	ethanol T = 298K; P = 50 psig
Rylander and Steele (14)	cinnamaldehyde crotonaldehyde acrolein	95% cinnamyl alcohol 90% crotyl alcohol 73% allyl alcohol	5% Os/Al_2O_3 and 5% Os/C	isopropanol or none T=373K; P=750-1000 psig
Khidekel et al. (15)	crotonaldehyde	90% crotyl alcohol	5% Ir/C	
Steiner (16)	β-methylcrotonaldehyde	91% unsaturated alcohol	250 mg PtO_2 and 15mg $Co(OAc)_3 \cdot 4H_2O$	solvent: n-butanol increase level of Co with more difficult selectivity problems
Ichikawa et al. (17)	β-methylcrotonaldehyde	93% unsaturated alcohol	Pt/PtO_2 with $FeSO_4$	P = 450 psig
Ichikawa et al. (18)	citral	96% citronellol	PtO_2 with Ni and Fe	P = 10 atm; T = 343K
Ichikawa and Teizo (19)	citral	83% citronellol	PtO_2 with Ni	

TABLE 1. (continued)

Vanderspurt (20,21)	acrolein	allyl alcohol	Re/supported	vapor phase, addition of CO or CS_2 increased selectivity to 60%
Jenck and Germain (22)	aldehydes ketones olefins	monofunctional cmpds; reactivities ald > ketone > olefin	Cu/Cr_2O_3	not applicable to conjugated cmpds; lower reactivity of carbonyl group
Hubaut et al. (23,24)	crotonaldehyde methacrolein methyl vinyl ketone	88% butyraldehyde 6% crotyl alcohol 6% butanol	Cu/Cr_2O_3	T = 313 K conversion = 26%
Sokolskii et al. (25)	crotonaldehyde	100% butyraldehyde 100% butyraldehyde 100% butyraldehyde 100% butyraldehyde 100% butyraldehyde 100% butyraldehyde 100% butyraldehyde	Pd black Pd black-SiO_2 Pd black-Al_2O_3 Pd black-B_2O_3 Pd black-MgO Pd black-Fe_2O_3 Pd black-ZnO	TOF = $0.033\ s^{-1}$ T = 293 K
Sokolskii et al. (26,27)	crotonaldehyde	80% crotyl alcohol 97% crotyl alcohol	Os black-Al_2O_3 Os black-ZnO	T = 293 K
Sokolskii et al. (26,27)	crotonaldehyde	60% butyraldehyde 10% crotyl alcohol 29% butanol	Ru black	T = 293 K 77% conversion TOF = $0.054\ s^{-1}$
Sokolskii et al. (26,27)	crotonaldehyde	61% butyraldehyde 13% crotyl alcohol 26% butanol	Ru black-Al_2O_3	T = 293 K 78% conversion

TABLE 1. (continued)

Sokolskii et al. (26,27)	crotonaldehyde	37% butyraldehyde 24% crotyl alcohol 39% butanol	Ru black-ZnO	T = 293 K 75% conversion
Sokolskii et al. (28)	crotonaldehyde	88% crotyl alcohol 12% 8% 66% 80% 0%	Os black-Fe_2O_3 Ru black-Fe_2O_3 Rh black-Fe_2O_3 Ir black-Fe_2O_3 Pt black-Fe_2O_3 Pd black-Fe_2O_3	T = 293 K solvent is water
Sokolskii et al. (28)	crotonaldehyde	56% crotyl alcohol 8% 0% 22% 0% 0%	Os black Ru black Rh black Ir black Pt black Pd black	T = 293 K solvent is water
Galvagno et al. (31)	acrolein	> 94 % propanal	10% Pt/C	T = 318 K; ethanol P = 1atm
Galvagno et al. (31)	acrolein	30% allyl alcohol	10% Pt/nylon	T = 318 K; ethanol P = 1atm
Galvagno et al. (31)	acrolein cinnamaldehyde	65% allyl alcohol 75% cinnamyl alcohol	Pt-Sn/nylon	T = 318 K; ethanol; P=1atm T = 333 K; ethanol
Galvagno et al. (32)	cinnamaldehyde	95% cinnamyl alcohol	Pt-Ge/nylon(1-7% Ge)	T = 333 K; ethanol; P= 1atm

TABLE 1. (continued)

Galvagno et al. (33)	cinnamaldehyde	< 10% cinnamyl alc.	Pt/nylon	T = 333K; ethanol P = 1atm
		< 10%	Pt-Na/nylon	
		< 10%	Pt-Ca/nylon	
		< 10%	Pt-Al/nylon	
		25% cinnamyl alcohol	Pt-Co/nylon	
		64% cinnamyl alcohol	Pt-Se/nylon	
		74% cinnamyl alcohol	Pt-Fe/nylon	
		75% cinnamyl alcohol	Pt-Sn/nylon	
		94% cinnamyl alcohol	Pt-Ge/nylon	
Galvagno et al. (34)	cinnamaldehyde	30% cinnamyl alcohol	0.5% Ru/C	T = 333K; ethanol P = 1atm
		35% cinnamyl alcohol	1% Ru/C	
		36% cinnamyl alcohol	2% Ru/C	
		47% cinnamyl alcohol	5% Ru/C	
		61% cinnamyl alcohol	10% Ru/C	
Galvagno et al. (36)	citral	36% gerinol + nerol 30% citronellal 10% isopulegol 14% citronellol	Ru/C	T = 333K; ethanol ~ 90% conversion P = 1atm
Galvagno et al. (37)	cinnamaldehyde	90% cinnamyl alcohol	RuSn/C Sn content: 30%	T = 333 K; ethanol 20-90% conversion P = 1atm
Goupil (38)	cinnamaldehyde	90% cinnamyl alcohol 30% (Pt/C)	Pt-Fe/C Fe content: 50%	T = 333 K; P_{H2}=4000kPa propanol, water and NaOAc

TABLE 1. (continued)

Giroir-Fendler et al. (41)	cinnamaldehyde	S^0	S^{25}	S^{50}				T = 333 K; P_{H2}=4MPa isopropanol, water, and NaOAc
		61%	72%	73%		Ir/G		
		60%	81%	81%		Ir/C		
		72%	78%	83%		Pt/G		
		0%	33%	55%		Pt/C		
		12%	39%	53%		Ru/G		
		0%	5%			Ru/C		
		0%	7%	24%		Rh/G		
		0%	0%	5%		Rh/C		
		0%	0%	0%		Pd/G		
		0%	0%	0%		Pd/C		
Richard et al. (42)	cinnamaldehyde	S^0	S^{25}	S^{50}	S^{75}			T = 333 K; P_{H2}=40 bars; isopropanol, water, and NaOAc
		32%	56%	68%	68%	4% Pt/C	Fe/Pt	
		64%	82%	88%	88%	4%Pt/C+$FeCl_2$	(0.1)	
		70%	80%	87%	87%	4%Pt/C+$FeCl_2$	(0.2)	
		69%	76%	83%	85%	4%Pt/C+$FeCl_2$	(0.3)	
		56%	82%	89%	86%	4%Pt/C+$FeCl_2$	(0.5)	
Gallezot et al. (43)	cinnamaldehyde	S^0	S^{25}	S^{50}	S^{75}			T = 333K; P_{H2}=40 bars; isopropanol, water, and NaOAc
		0%	74%	82%	82%	Pt/Y		
		0%	16%	30%	22%	Rh/Y		

TABLE 1. (continued)

Giroir-Fendler et al. (44)	cinnamaldehyde	S^0 S^{25} S^{50} S^{75} 12% 14% 18% 20% 32% 36% 42% 45% 72% 78% 83% 91% 96% 98% 74% 76% 72% 73% 74% 81% 90% 90% 93%	$D_{particle(nm)}$ Rh/G1 2.5 Rh/G2 7 Pt/G1 1.3 Pt/G2 5 Pt/Al_2O_3 4-6 PtAd1 2-6 PtAd2 20-200	Same conditions as above. P_{H2}=4 MPa G1 (T_{redn} = 573K;2hr) G2 (T_{redn} = 773K H_2 and 1173K vacuum Pt-Adatoms PtAd1 (T_{redn} = 333K) PtAd2 (T_{redn} = 373K)
Nitta et al. (45)	cinnamaldehyde	S^0 = 90% S^{50} = 80% cinnamyl alcohol	Co/SiO_2 D_c=17nm	T = 303 K; ethanol T_{redn} = 700°C; 1hr P_{H2}=1kg/cm^2
Nitta et al. (45)	cinnamaldehyde	S^0 = 83% S^{50} = 78% cinnamyl alcohol	Co/SiO_2 D_c=13nm	T = 303 K; ethanol T_{redn} = 600°C; 1hr P_{H2}=10kg/cm^2
Nitta et al. (45)	cinnamaldehyde	S^0 = 86% S^{50} = 75% cinnamyl alcohol	Co/SiO_2 D_c=9nm	T = 303 K; ethanol T_{N2}= 500°C; 1hr; T_{redn}=600°C; 1hr P_{H2}=10kg/cm^2
Nitta et al. (45)	cinnamaldehyde	S^0 = 89% S^{50} = 79% cinnamyl alcohol	Co/SiO_2; different catalyst prep. D_c=18nm	T = 303 K; ethanol T_{redn} = 600°C; 1hr P_{H2}=10kg/cm^2
Nitta et al. (45)	cinnamaldehyde	S^0 = 94% S^{50} = 91% cinnamyl alcohol	Co/SiO_2; ppt. from $CoCl_2$ D_c=18nm	T = 303 K; ethanol T_{redn} = 400°C; 2hr P_{H2}=1kg/cm^2
Nitta et al. (45)	crotonaldehyde	S^0 = 42% S^{50} = 30% crotyl alcohol	Co/SiO_2 D_c=13nm	T = 303 K; ethanol T_{redn} = 600°C; 1hr P_{H2}=1kg/cm^2

TABLE 1. (continued)

Nitta et al. (45)	crotonaldehyde	$S^0 = 76\%$ $S^{50} = 65\%$ crotyl alcohol	Co/SiO_2; different catalyst prep. D_c=18nm	T = 303 K; ethanol T_{redn} = 600°C; 1hr P_{H2}=10kg/cm^2
Nitta et al. (45)	crotonaldehyde	$S^0 = 75\%$ $S^{50} = 61\%$ crotyl alcohol	Co/SiO_2; ppt. from $CoCl_2$ D_c=18nm	T = 303 K; ethanol T_{redn} = 400°C; 2hr P_{H2}=1kg/cm^2
Nitta et al. (77)	cinnamaldehyde	$S^0 = 94\%$ $S^{50} = 93\%$ cinnamyl alcohol	Co/SiO_2; chloride salt D_c=18nm Dried 110°C;10hr	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr
Nitta et al. (77)	cinnamaldehyde	$S^0 = 81\%$ $S^{50} = 77\%$ cinnamyl alcohol	Co/SiO_2; nitrate salt D_c=7nm Dried 110°C;10hr	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr
Nitta et al. (77)	cinnamaldehyde	$S^0 = 76\%$ $S^{50} = 68\%$ cinnamyl alcohol	Co/SiO_2; acetate salt D_c<4nm Dried 110°C;10hr	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr
Nitta et al. (77)	cinnamaldehyde	$S^0 =98\%$ $S^{50} = 96\%$ cinnamyl alcohol	Co/SiO_2; chloride salt D_c=7-9nm Dried 120°C;44hr	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr
Nitta et al. (77)	cinnamaldehyde	$S^0 =78\%$ $S^{50} = 71\%$ cinnamyl alcohol	Co/SiO_2; nitrate salt D_c=6nm Dried 120°C;44hr	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr
Nitta et al. (77)	cinnamaldehyde	$S^0 = 80\%$ $S^{50} = 59\%$ cinnamyl alcohol	Co/SiO_2; acetate salt D_c=4-5nm Dried 120°C;44hr	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr
Nitta et al. (77)	cinnamaldehyde	$S^0 = 98\%$ $S^{50} = 96\%$ cinnamyl alcohol	Co/SiO_2; chloride salt D_c=7-9nm Dried 120°C;44hr	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr

TABLE 1. (continued)

Nitta et al. (77)	crotonaldehyde	S^{50} = 25% crotyl alc	Co/TiO_2; nitrate salt D_c=17nm	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 350°C; 1hr
Nitta et al. (77)	crotonaldehyde	S^{50} = 80% crotyl alc	Co/TiO_2; chloride salt D_c=31nm	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 350°C; 1hr
Nitta et al. (77)	crotonaldehyde	S^{50} = 32% crotyl alc	Co/SiO_2; nitrate salt D_c=8nm silica gel no. 1	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr
Nitta et al. (77)	crotonaldehyde	S^{50} = 80% crotyl alc	Co/SiO_2; chloride salt D_c=9nm silica gel no. 1	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 400°C; 2hr
Nitta et al. (77)	crotonaldehyde	S^{50} = 32% crotyl alc	Co/Al_2O_3; nitrate salt D_c=22nm	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 350°C; 1hr
Nitta et al. (77)	crotonaldehyde	S^{50} = 74% crotyl alc	Co/Al_2O_3; chloride salt D_c=29nm	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 350°C; 1hr
Nitta et al. (77)	crotonaldehyde	S^{50} = 28% crotyl alc	Co/ZrO_2; nitrate salt D_c=16nm	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 350°C; 1hr
Nitta et al. (77)	crotonaldehyde	S^{50} = 24% crotyl alc	Co/C; nitrate salt D_c=25nm	T = 303 K; ethanol P_{H2} = 1 MPa T_{redn} = 350°C; 1hr
Blackmond et al. (46)	3-methyl crotonaldehyde	S^{41} = 12% unsatd alc S^{39} = 34% unsatd alc	Ru/NaY Ru/KY	liquid phase; isopropanol; T=373K; P_{H2} =4MPa

TABLE 1. (continued)

Blackmond et al. (46)	3-methyl crotonaldehyde	42%- 32%↓ with time	Ru/NaY	gas phase; T=313K; P_{H2}=0.1MPa
		50% unsatd alc	Ru/KY	
Blackmond et al. (47)	cinnamaldehyde	S^{25} cinnamyl alcohol		T = 373K; P_{H2} = 4 MPa; isopropanol
		30%	Ru/C	
		63%	Ru/NaY	
		67%	Ru/KY	
		68%	Pt/NaY	
		60%	Pt/KY	
		30%	Rh/NaY	
		33%	Rh/KY	
Blackmond et al. (47)	3-methyl crotonaldehyde	S^{25} unsatd alcohol		T = 373K; P_{H2} = 4 MPa; isopropanol
		26%	Ru/C	
		10%	Ru/NaY	
		35%	Ru/KY	
		42%	Pt/NaY	
		56%	Pt/KY	
		6%	Rh/NaY	
		10%	Rh/KY	
Blackmond et al. (49)	3-methyl crotonaldehyde	100% satd aldehyde	Ru black	Conversions < 5% @ T = 343K
		100% satd aldehyde	Ru/SiO_2	
Waghray et al. (50)		70% unsatd alcohol	RuK/SiO_2	T = 313-393K
		38%	Ru/NaY	
		55%	Ru/KY	
		65%	Ru/CsY	

TABLE 1. (continued)

Blackmond and Waghray (51)	3-methyl crotonaldehyde	8% 75% 80% 55% 4%	Ru/SiO_2 Ru-10%K/SiO_2 Ru-20%K/SiO_2 10%K-Ru/SiO_2 Ru-10%K/SiO_2	T = 313 K Ru imp. SiO_2 then K Ru imp. SiO_2 then K K imp. SiO_2 then Ru physical mixture
Simonek and Beranek (48)	crotonaldehyde		1%Pt-0.4%Fe-0.06%Zn/charcoal 1%Pt0.7%Fe/silica gel + 2%NaOH	$T = 433$ K; $P \leq 1$ atm
Vannice and Sen (54)	crotonaldehyde	100% butyraldehyde	5% Pt/SiO_2 $E_{act} = 3$ kcal/mol	T = 319 K; P = 1atm H_2/croald = 22.7; TOF = 0.044 s^{-1} 20% conversion
Vannice and Sen (54)	crotonaldehyde	100% butyraldehyde	2.1% Pt/Al_2O_3 $E_{act} = 4$ kcal/mol	T = 317 K; P = 1atm H_2/croald = 22.7; TOF = 0.047 s^{-1} 10% conversion
Vannice and Sen (54)	crotonaldehyde	14% crotyl alcohol	4.6%Pt/TiO_2 T_{redn} =473 K $E_{act} = 8$ kcal/mol	T = 319 K; P = 1atm H_2/croald = 22.7; TOF = 0.024 s^{-1} 30% conversion
Vannice and Sen (54)	crotonaldehyde	37% crotyl alcohol	1.9%Pt/TiO_2 T_{redn} =773 K $E_{act} = 7$ kcal/mol	T = 318 K; P = 1atm H_2/croald = 22.7; TOF = 1.68 s^{-1} 12% conversion

TABLE 1. (continued)

Vannice and Sen (54)	butyraldehyde	butanol TOF E_{act} 0.051 0.098 0.10 10 2.6 10	0.7%Pt/SiO_2 2.1%Pt/Al_2O_3 1.9%Pt/TiO_2(LTR) 1.9%Pt/TiO_2(HTR)	T = 353K, P_{total} =1 atm; H_2/butald = 24.5 TOF (s^{-1}) E_{act} (kcal/mol)
Vannice and Sen (54)	crotyl alcohol	butald TOF E_{act} 0.030 7 0.010 4 0.010 1.50 6	0.7%Pt/SiO_2 2.1%Pt/Al_2O_3 1.9%Pt/TiO_2(LTR) 1.9%Pt/TiO_2(HTR)	T = 353K, P_{total} = 1 atm; H_2/croalc = 31 TOF (s^{-1}) E_{act} (kcal/mol)
Vannice and Sen (54)	crotyl alcohol	butanol TOF E_{act} 0.53 2 0.133 3 0.104 6.5 3	0.7%Pt/SiO_2 2.1%Pt/Al_2O_3 1.9%Pt/TiO_2(LTR) 1.9%Pt/TiO_2(HTR)	T = 353K, P_{total} = 1 atm; H_2/butald = 24.5 TOF (s^{-1}) E_{act} (kcal/mol)
Yoshitake (57)	acrolein	preferential formation of allyl alc at T=353K over HTR catalyst	Ir/Nb_2O_5 (LTR)473K Ir/Nb_2O_5 (HTR)773K	$E_{act(propanal\ \&\ allyl\ alcohol)}$=12kJ/mol(LTR) $E_{act(propanal)}$=35kJ/mol (HTR) $E_{act(allyl\ alc)}$ = 5kJ/mol(HTR)
Wismeijer (59)	crotonaldehyde		5% Ru/SiO_2	T = 303 K; P_{H2} = 101 kPa; cyclohexane TOF = 0.0014 s^{-1}
Wismeijer (59)	crotonaldehyde		1% Ru/TiO_2	T = 303 K; P_{H2} = 101 kPa; cyclohexane TOF = 0.011 s^{-1}

TABLE 1. (continued)

Wismeijer (60)	citronellal	50% citronellol ↑ with an ↑ in T_{act}	5% Ru/SiO_2 T_{act} = 873 K	T = 303 K; P_{H2} = 101 kPa; cyclohexane TOF =0.055 s^{-1}
Wismeijer (60)	citronellal	90% citronellol	1% Ru/SiO_2 T_{act} = 773 K	T = 303 K; P_{H2} = 101 kPa; cyclohexane TOF = 0.034-0.32 s^{-1} (↑ with ↑ T_{act})
Kaspar (61)	crotonaldehyde	S^{100} = 0% crotyl alc S^{100} = 0% S^{100} = 0% S^{100} = 0% S^{52} = 14% S^{25} = 11% S^{73} = 11% S^{29} = 14%	Rh/TiO_2 (HTR) Rh/TiO_2 (LTR) Ru/TiO_2 (HTR) Ru/TiO_2 (LTR) Os/TiO_2 (HTR) Os/TiO_2 (LTR) Ir/TiO_2 (HTR) Ir/TiO_2 (LTR)	T = 373 K 50 mg catalyst
Touroude (63)	crotonaldehyde	P_{H2}/P_{croald} 25% crotyl alc 95 22% crotyl alc 60 19% crotyl alc 30	4.7% Pt/TiO_2	T = 333K T_{redn} = 200°C
Raab and Lercher (64)	crotonaldehyde	S^{10} TOF 0% crotyl alc .03 5.9% .07 2.9% .45 2.6% .57 2.6% .60 2.4% .50 1.6% .66 0% .72	$E_{a(kJ/mol)}$ Pt/SiO_2 42 $.1Ni\text{-}.9Pt/SiO_2$ 43 $.3Ni\text{-}.7Pt/SiO_2$ 42 $.5Ni\text{-}.5Pt/SiO_2$ 43 $.7Ni\text{-}.3Pt/SiO_2$ 45 $.8Ni\text{-}.2Pt/SiO_2$ 47 $.9Ni\text{-}.1Pt/SiO_2$ 47 Ni/SiO_2 50	T=353-413K; P=1atm P_{H2} = 949 mbar P_{croald} = 64 mbar 1-10 mg catalyst TOF (mol/s*H_{ads})

TABLE 1. (continued)

Raab et al. (65)	crotonaldehyde	$S^{<10}$	TOF				$E_{a(kJ/mol)}$	T=353-413K; P=1atm
		0% crotyl alc	.03			Pt/SiO$_2$	42	P_{H2} = 953 mbar
		2.0%	.45			PtNi/SiO$_2$	42	P_{croald} = 60 mbar
		56.4%	.43			PtGa/SiO$_2$	33	1-10 mg catalyst
		30.9%	.36			PtSn/SiO$_2$	27	TOF (mol/s*H_{ads})
		46.3%	.29			Pt/TiO$_2$	46	
Raab and Lercher (67)	crotonaldehyde	S^5	TOF	$E_{a(UOL)}$			$E_{a(kJ/mol)}$	T=353-413K; P=1atm
		46.3%	.29	25		Pt/TiO$_2$	28	P_{H2} = 953 mbar
		30.6%	.49	27		.1Ni-.9Pt/TiO$_2$	29	P_{croald} = 60 mbar
		14.9%	.94	30		.3Ni-.7Pt/TiO$_2$	39	1-10 mg catalyst
		8.2%	.84	14		.5Ni-.5Pt/TiO$_2$	27	TOF (molec/s*H_{ads})
		4.5%	1.22	16		.7Ni-.3Pt/TiO$_2$	53	
		2.5%	1.32	20		.9Ni-.1Pt/TiO$_2$	54	
		0.3%	0.21			Ni/TiO$_2$	74	
Marinelli et al. (69,70)	acrolein	~100% propanal				5%Ni/SiO$_2$		T = 353K
		~100% propanal				Ni-Cu/SiO$_2$		P_{H2} = 978 mbar
		1.6% allyl alcohol				5%Pt/SiO$_2$		$P_{acrolein}$ = 33 mbar
		3.6-4.6% allyl alcohol				Pt-Cu/SiO$_2$		5% Pt; Pt:X = 4:1
		3.6-4.6% allyl alcohol				Pt-S/SiO$_2$		
Marinelli et al. (69,70)	acrolein	S_{sal}	S_{uol}	S_{sol}	S_{HC}	5% Pt; Pt:X = 4:1		T = 353K
		92.6%	1.6	1.8	4	5%Pt/SiO$_2$		P_{H2} = 978 mbar
		96.9%	0.9	1.2	1	Pt-Na/SiO$_2$		$P_{acrolein}$ = 33 mbar
		89.7%	4.2	2.8	3.3	Pt-Ti/SiO$_2$		
		90%	3.4	3.1	3.5	Pt-V/SiO$_2$		
		84.9%	7.3	7.4	0.4	Pt-Fe/SiO$_2$		
		75.6%	13.2	8.4	2.8	Pt-Ga/SiO$_2$		
		90.7%	3.2	1.6	4.5	Pt-Ge/SiO$_2$		
		67%	27.5	2.9	2.6	Pt-Sn/SiO$_2$		

TABLE 1. (continued)

Marinelli et al. (69,70)	crotonaldehyde	S_{sal}	S_{uol}	S_{sol}	S_{HC}	5% Pt; Pt:X = 4:1	T = 353K P_{H2} = 978 mbar P_{croald} = 33 mbar
		50.0%	13.0	33.6	3.4	5%Pt/SiO_2	
		62.5%	9.0	25.9	2.6	Pt-Na/SiO_2	
		45%	18.2	33.6	3.2	Pt-Ti/SiO_2	
		67.4%	11.5	17.4	3.6	Pt-V/SiO_2	
		44.9%	27.8	26.1	1.2	Pt-Fe/SiO_2	
		40.3%	25.1	33.5	1.1	Pt-Ga/SiO_2	
		49.1%	11.9	36.4	2.7	Pt-Ge/SiO_2	
		50.1%	29.5	19.4	1.0	Pt-Sn/SiO_2	
Marinelli et al. (69,70)	3-methyl crotonaldehyde	S_{sal}	S_{uol}	S_{sol}	S_{HC}	5% Pt; Pt:X = 4:1	T = 353K P_{H2} = 978 mbar $P_{3methcroald}$ = 33 mbar
		17.0%	20.5	55.0	7.5	5%Pt/SiO_2	
		36.9%	13.4	48.6	1.1	Pt-Na/SiO_2	
		18.8%	33.7	44.5	3.0	Pt-Ti/SiO_2	
		19.5%	27.4	50.6	2.5	Pt-V/SiO_2	
		5.1%	80.4	14.4	0.1	Pt-Fe/SiO_2	
		4.3%	67.1	28.1	0.5	Pt-Ga/SiO_2	
		20.9%	19.4	53.1	6.6	Pt-Ge/SiO_2	
		7.6%	77.5	14.9	0.0	Pt-Sn/SiO_2	
Marinelli et al. (69,70)	methacrolein	S_{sal}	S_{uol}	S_{sol}	S_{HC}	5% Pt; Pt:X = 4:1	T = 353K P_{H2} = 978 mbar $P_{methacrolein}$ = 33 mbar
		88.3%	2.2	3.0	6.4	5%Pt/SiO_2	
		96.2%	0.8	1.3	1.7	Pt-Na/SiO_2	
		83.3%	8.2	4.8	3.7	Pt-Ti/SiO_2	
		83.8%	6.7	6.2	3.3	Pt-V/SiO_2	
		79%	6.6	13.4	1.1	Pt-Fe/SiO_2	
		70.3%	14.9	12.9	1.8	Pt-Ga/SiO_2	
		67.5%	20.4	9.6	2.6	Pt-Ge/SiO_2	
		61.3%	26.3	11.4	0.9	Pt-Sn/SiO_2	

TABLE 1. (continued)

Marinelli et al. (69,70)	methyl vinyl ketone	S_{sal}	S_{uol}	S_{sol}	S_{HC}	5% Pt; Pt:X = 4:1	T = 353K P_{H2} = 978 mbar P_{MVK} = 33 mbar
		96.6%	0.1	3.2	0.1	5%Pt/SiO_2	
		88.1%	0.0	11.8	0.1	Pt-Na/SiO_2	
		94.5%	0.2	5.3	0.0	Pt-Ti/SiO_2	
		90.8%	0.0	9.1	0.1	Pt-V/SiO_2	
		83.8%	0.2	15.9	0.1	Pt-Fe/SiO_2	
		91.3%	0.2	8.1	0.4	Pt-Ga/SiO_2	
		94.9%	0.3	4.7	0.1	Pt-Ge/SiO_2	
		96.2%	0.1	3.6	0.1	Pt-Sn/SiO_2	
Marinelli et al. (69)	acrolein	1.5% allyl alcohol				5%Pt/SiO_2	T = 353K P_{H2} = 978 mbar $P_{acrolein}$ = 33 mbar 5% Pt; Pt:Sn = 4:1
		17%				5%PtSn/SiO_2(10%Sn)	
		25%				5%PtSn/SiO_2(20%Sn)	
		22%				5%PtSn/SiO_2(25%Sn)	
Marinelli (PhD dissertation)	acrolein	S_{sal}	S_{uol}	S_{sol}	S_{HC}		severe presulfurization;20ml/ min of thiophene/H_2 (1/12) over reduced catalyst at 570K 3hr
		80.5%	6.3	7.1	6.1	5%Pt/SiO_2	
		87.4%	2.2	3.0	7.4	5%Pt/Al_2O_3	
		72.8%	3.3	4.1	19.7	5%Cu/SiO_2	
		79.5%	6.4	8.3	5.8	5%Cu/Al_2O_3	
Marinelli (PhD dissertation)	acrolein	S_{sal}	S_{uol}	S_{sol}	S_{HC}		mild presulfurization;5ml/ min of thiophene/H_2 (1/43) over reduced catalyst at 298K for 1/2 min
		81.9%	5.8	8.2	4.1	5%Pt/SiO_2	
		88.5%	4.7	4.2	2.6	5%Pt/Al_2O_3	
		77.0%	2.6	3.0	17.3	5%Cu/SiO_2	
		76.5%	2.7	3.9	16.9	5%Cu/Al_2O_3	

TABLE 1. (continued)

Marinelli (PhD dissertation)	acrolein	S_{sal} S_{uol} S_{sol} S_{HC} 84.2% 5.1 6.5 4.2 87.6% 5.0 4.5 3.0 78.2% 2.2 3.2 16.3 76.5% 7.2 11.2 5.0	5%Pt/SiO_2 5%Pt/Al_2O_3 5%Cu/SiO_2 5%Cu/Al_2O_3	1 μl of liquid thiophene on the reduced catalyst
Marinelli (PhD dissertation)	acrolein	S_{sal} S_{uol} S_{sol} S_{HC} 79.9% 2.9 4.0 13.1 80.6% 3.5 4.5 11.4 93.7% 0.0 0.0 6.3 91.5% 1.3 1.3 5.9	5%Pt/SiO_2 5%Pt/Al_2O_3 5%Cu/SiO_2 5%Cu/Al_2O_3	no sulfurization
Hutchings et al. (73)	crotonaldehyde	< 10% crotyl alcohol > 50% crotyl alcohol (max. selectivity = 64% crotyl alcohol)	5%Cu/Al_2O_3 (no S) 5%Cu/Al_2O_3	T = 353 K - 423K H_2/croald = 14 1 μl thiophene/0.1 g catalyst
Beccat et al. (75)	crotonaldehyde	TOF E_a S croalc 0.6 46 0.1 butald 5.6 48 croalc 2.9 25 .13 butald 20 33	Pt(111) $Pt_{80}Fe_{20}$(111)	T = 330 K; P_{H2} = 3 Pa TOF ($10^{-2}s^{-1}$per surface atom); $E_{a(kJ/mol)}$
Beccat et al. (75)	methyl-crotonaldehyde	TOF E_a S uol 2.3 23 .56 ual 1.8 46 uol 13 34 .70 ual 5.5 50	Pt(111) $Pt_{80}Fe_{20}$(111)	T = 330 K; P_{H2} = 3 Pa TOF ($10^{-2}s^{-1}$per surface atom); $E_{a(kJ/mol)}$
Beccat et al. (75)	butyraldehyde	TOF E_a butanol 0.2 54 butanol 3.1 42	Pt(111) $Pt_{80}Fe_{20}$(111)	T = 330 K; P_{H2} = 3 Pa TOF ($10^{-2}s^{-1}$per surface atom); $E_{a(kJ/mol)}$

TABLE 1. (continued)

Beccat et al. (75)	crotyl alcohol	TOF E_a butanol 27 29 butanol 67 35	Pt(111) $Pt_{80}Fe_{20}(111)$	T = 330 K; P_{H2} = 3 Pa TOF ($10^{-2}s^{-1}$per surface atom); $E_{a(kJ/mol)}$
Beccat et al. (75)	methyl-butyraldehyde	TOF E_a mebutnol .35 50 mebutnol 5.3 52	Pt(111) $Pt_{80}Fe_{20}(111)$	T = 330 K; P_{H2} = 3 Pa TOF ($10^{-2}s^{-1}$per surface atom); $E_{a(kJ/mol)}$
Beccat et al. (75)	methyl-crotyl alcohol	TOF E_a mebutnol 1.6 44 mebutnol 7 44	Pt(111) $Pt_{80}Fe_{20}(111)$	T = 330 K; P_{H2} = 3 Pa TOF ($10^{-2}s^{-1}$per surface atom); $E_{a(kJ/mol)}$
Noller and Lin (76)	crotonaldehyde	14% butyraldehyde 0% crotyl alcohol 86% butanol	16.67%NiO/Al_2O_3	T = 353 K 100% conversion
Noller and Lin (76)	crotonaldehyde	100% butyraldehyde	22.5%CuO/Al_2O_3	T = 353 K 10% conversion
Noller and Lin (76)	crotonaldehyde	12% butyraldehyde 54% crotyl alcohol 33% butanol	21%NiO-10%CuO/Al_2O_3	T = 353 K 100% conversion
Coq et al. (78)	acrolein	TOF (h^{-1}) $S_{allyl\ alc}$ 81.6 27.4 11.5 25.8 9.5 31.4 43.4 59.3	0.20%Pt/Al_2O_3 1.3%Ir/Al_2O_3 1.05%Ru/Al_2O_3 0.81%Ni/Al_2O_3 0.45%Co/Al_2O_3	T = 363 K; P = 1 atm $P_{acrolein}$ = 11 kPa P_{H2} = 9 kPa P_{N2} = 81kPa t = 3 min on stream

TABLE 1. (continued)

Coq et al. (78)	acrolein	TOF (h^{-1})	$S_{allyl\ alc}$			T = 363 K; P = 1 atm
		39.8	3.4	0.20%Pt/Al_2O_3		$P_{acrolein}$ = 11 kPa
		4.0	5.3	1.3%Ir/Al_2O_3		P_{H2} = 9 kPa
		10.1	7.3	1.05%Ru/Al_2O_3		P_{N2} = 81kPa
			5.3	0.81%Ni/Al_2O_3		t = 120min on stream
			11.0	0.45%Co/Al_2O_3		
Coq et al. (78)	acrolein	TOF (h^{-1})	$S_{allyl\ alc}$		$P_{size(nm)}$	T = 363 K; P = 1 atm
		95.9	34.5	.86% Ru/Al_2O_3	>10	$P_{acrolein}$ = 11 kPa
		15.5	37.7	.68% Ru/Al_2O_3		P_{H2} = 9 kPa
		6.2	45.2	1.1% Ru/Al_2O_3	1.95	P_{N2} = 81kPa
		9.5	31.4	1.05% Ru/Al_2O_3	1.1	t = 3 min on stream
		11.0	39.6	.68% Ru/Al_2O_3	1.1	
		25.8	21.3	.18% Ru/Al_2O_3	1.0	
Coq et al. (78)	acrolein	TOF (h^{-1})	$S_{allyl\ alc}$		$P_{size(nm)}$	T = 363 K; P = 1 atm
		9.50	31.4	1.05% Ru/Al_2O_3	1.1	$P_{acrolein}$ = 11 kPa
		6.2	45.2	1.1% Ru/Al_2O_3	1.95	P_{H2} = 9 kPa
		62.7	10.9	1.1%Ru/$TiO_{2(LTR)}$	1.03	P_{N2} = 81kPa
		1300	37.7	1.1%Ru/$TiO_{2(HTR)}$		t = 3 min on stream
		151	57.1	1.29%Ru/SiO_2	1.4	
		23.4	74.3	1.2% Ru/ZrO_2	1.7	
		88.3	3.3	0.9% Ru/G		
Coq et al. (79)	acrolein	TOF (h^{-1})	$S_{allyl\ alc}$			T = 363 K; P = 1 atm
		6.2	45.2	1.1% Ru/Al_2O_3		$P_{acrolein}$ = 11 kPa
		25.7	52.7	1.1%Ru.29%Sn/Al_2O_3		P_{H2} = 9 kPa
		27.9	42.7	1.1%Ru.14%Fe/Al_2O_3		P_{N2} = 81kPa
		45.5	17.1	1.1%Ru.17%Ge/Al_2O_3		
		53.1	7.1	1.1%Ru.30%Sb/Al_2O_3		
		45.8	7.4	1.1%Ru.16%Zn/Al_2O_3		

TABLE 1. (continued)

Coq et al. (80)	cinnamaldehyde	TOF	S^0	S^{10}	S^{25}		$P_{size(nm)}$	T = 383 K; *i*-propanol
		29.8	80.2	74	75	Ru sponge		P_{H2} = 4.5 MPa
		12.8	48	55	60	.86% Ru/Al_2O_3	>10	TOF = $(h^{-1}) \times 10^{-2}$
		4.16	30	47.1	52	4%Ru/Al_2O_3		
		3.86	23	41.6	50	.68% Ru/Al_2O_3	2.7	
		1.48	22	42	55	1.1% Ru/Al_2O_3	1.9	
		2.34	23	41.3	55	1.05% Ru/Al_2O_3	1.1	
		1.81	23.3	44.4	56	.68% Ru/Al_2O_3	1.1	
Coq et al. (80)	cinnamaldehyde	TOF	S^0	S^{25}	S^{50}			T = 383 K; *i*-propanol
		1.48	22	55	52	1.1% Ru/Al_2O_3		P_{H2} = 4.5 MPa
		7.13	46.8	60	63.6	1.1%Ru-Sn/Al_2O_3		TOF = $(h^{-1}) \times 10^{-2}$
		3.08	46.3	57.5	59	1.1%Ru-Ge/Al_2O_3		
		4.40	37.3	54.8	57.2	1.1%Ru-Zn/Al_2O_3		
		3.86	47	53	55.2	1.1%Ru-Sb/Al_2O_3		
		9.15	42	52.1	57	1.1%Ru-Fe/Al_2O_3		
		2.95	49.2	53		1.1%Ru-Ag/Al_2O_3		
Coq et al. (80)	cinnamaldehyde	TOF	S^0	S^{25}	S^{50}		$P_{size(nm)}$	T = 383 K; *i*-propanol
		7.34	39	61	65	1.29%Ru/SiO_2	1.4	P_{H2} = 4.5 MPa
		72.6	66	75	76	0.9% Ru/G		TOF = $(h^{-1}) \times 10^{-2}$
		3.56				1.1%Ru/$TiO_{2(LTR)}$	1.05	
		291				1.1%Ru/$TiO_{2(HTR)}$	1.25	
		23.0	55	69	74	1.1%Ru/$TiO_{2(HTR)}$	1.25	Ru/TiO_2(HTR) T_{rxn} =
		3.13	60	69	70	1.2% Ru/ZrO_2 A	1.7	333K
		1.13	51.7	60	60	1.0% Ru/ZrO_2 T	2.1	A = amorphous

TABLE 1. (continued)

Coq et al. (81)	cinnamaldehyde	TOF	S^0	S^{25}	S^{50}		$P_{size(nm)}$	T = 383 K; *i*-propanol
		84	52	61	61	1.01%Ru573/ZrO_2	2.1	P_{H2} = 4.5 MPa
		135	54	61	65	1.01%Ru773/ZrO_2	2.1	TOF = (h^{-1})
		119	54	53	52	1.01%Ru973/ZrO_2	4-6	
		239	60	69	72	1.2%Ru623/ZrO_2^A	1.7	A = amorphous
		133	22	55	52	1.1% Ru/Al_2O_3	2.0	
Coq et al. (81)	cinnamaldehyde	TOF	S^0	S^{25}	S^{50}		$P_{size(nm)}$	T = 383 K; *i*-propanol
		84	52	61	61	Ru573/ZrO_2	2.1	P_{H2} = 4.5 MPa
		136	65	72.5	74	Ru573Sn/ZrO_2 (1)	1.9	TOF = (h^{-1})
		133	61	62	65	Ru573Sn/ZrO_2 (2)	2.0	Ru wt% = 1.01%
		76	66	72.5	75.5	Ru573Sn/ZrO_2 (3)	2.2	(1) .27%Sn, (2).38%Sn,
		135	52	55	55	Ru573Fe/ZrO_2 (4)		(3).53%Sn, (4).15%Fe

TABLE 2. Structural examples of α, β unsaturated aldehydes and the products formed upon hydrogenation

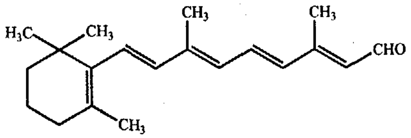
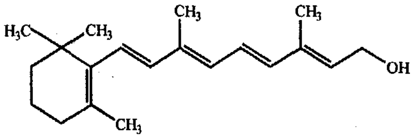
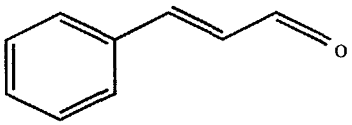
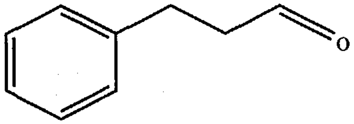
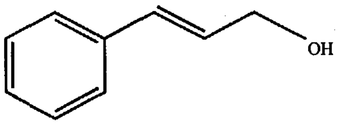
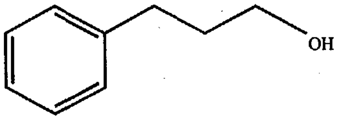
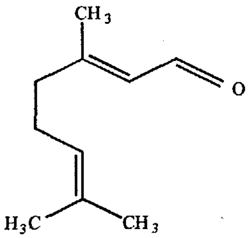
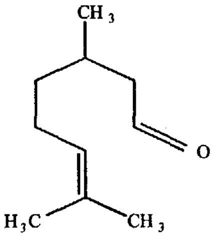
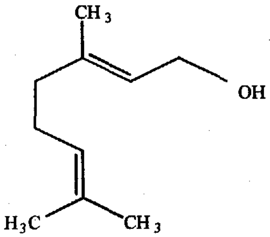
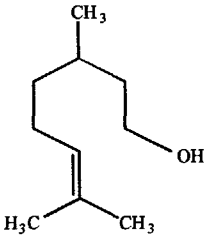
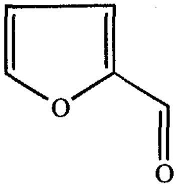
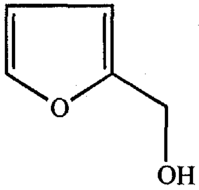
α, β Unsaturated Aldehyde	**Saturated Aldehyde**	**Unsaturated Alcohol**	**Saturated Alcohol**
 all trans retinal		 retinol (Vitamin A)	
 cinnamaldehyde	 hydrocinnamaldehyde	 cinnamyl alcohol	 phenyl propanol
 citral	 citronellal	 geraniol	 citronellol
 furfural		 furfuryl alcohol	

TABLE 2. (continued)

$(CH_3)_2C{=}CHCHO$ 3-methyl crotonaldehyde 3-methyl-2-butenal	$(CH_3)_2CHCH_2CHO$ isovaleraldehyde 3-methyl butanal	$(CH_3)_2C{=}CHCH_2OH$ 3-methyl-2-buten-1-ol	$(CH_3)_2CHCH_2CH_2OH$ isoamyl alcohol 3-methyl-1-butanol
$CH_3CH{=}CHCHO$ crotonaldehyde 2-butenal	$CH_3CH_2CH_2CHO$ butyraldehyde butanal	$CH_3CH{=}CHCH_2OH$ crotyl alcohol 2-buten-1-ol	$CH_3CH_2CH_2CH_2OH$ 1-butanol
$CH_2{=}C(CH_3)CHO$ methacrolein methacrylaldehyde	$(CH_3)_2CHCHO$ isobutyraldehyde 2-methyl propanal	$CH_2{=}C(CH_3)CH_2OH$ 2-methyl-2-propen-1-ol	$(CH_3)_2CHCH_2OH$ isobutyl alcohol 2-methyl-1-propanol
$CH_2{=}CHCH{=}O$ acrolein 2-propenal	$CH_3CH_2CH{=}O$ propionaldehyde propanal	$CH_2{=}CHCH_2OH$ allyl alcohol 2-propen-1-ol	$CH_3CH_2CH_2OH$ 1-propanol

TABLE 3. Summary of proposed catalytic effects for increased selectivity to the unsaturated alcohol

RESEARCHER	REACTANT	CATALYST	PROPOSED EFFECTS FOR INCREASED SELECTIVITY
Galvagno et al. (31,32)	acrolein cinnamaldehyde	Pt-Sn/nylon	• site blocking and/or electronic interaction between Pt and Sn • activates the carbonyl group: increases the polarization charge of the $C=O$ group which facilitates the transfer of hydrogen from adjacent sites
Goupil et al. (38-39)	cinnamaldehyde	Pt-Fe/C	saturated aldehyde remains adsorbed on surface • steric effect: molecule is forced to adsorb end-on via the $C=O$ group • electronic effect: increase in charge density of metal which would lower the probability for $C=C$ activation
Giroir-Fendler et al. (40-43)	cinnamaldehyde	Pt/G, Rh/G, Ru/G	• electronic effect: transfer in charge from support to metal which increases charge density of Pt therefore lowering the probability of $C=C$ bond activation
Richard et al. (42)	cinnamaldehyde	Pt-Fe/C	Dual site mechanism (electronic effect) • Fe preferentially activates the $C=O$ group (Fe adatoms carry a positive charge) • Pt sites provide hydrogen for hydrogenation of the $C=O$ group
Giroir-Fendler et al. (44)	cinnamaldehyde	Rh/G, Pt/G Pt-Adatoms	Geometric effects: • morphology of the metal particles • steric configuration of the molecules

TABLE 3. (continued)

Blackmond et al. (46-47)	3-methyl crotonaldehyde	Ru/NaY, Ru/KY, Pt/NaY, Pt/KY, Rh/NaY, Rh/KY	Dual site mechanism proposed by Richard et al.(42) • cationic sites to activate the C=O group • metallic sites to provide hydrogen
Blackmond et al. (47)	cinnamaldehyde	Ru/NaY, Ru/KY, Pt/NaY, Pt/KY, Rh/NaY, Rh/KY, Ru/C	• zeolite pore structure (bulkiness of phenyl group and rigidity of the side chain) • not the electronic properties of the cation
Blackmond et al. (49-52)	3-methyl crotonaldehyde	RuK/SiO_2	• K blocks the low coordination Ru sites • sites at Ru-K interface active for C=O hydrogenation • degree of closeness of the promoter to the catalytically active Ru sites is an important factor • a surface covered with a variety of adsorbed reactants, products and organic fragments
Vannice et al. (54-56)	crotonaldehyde	Pt/TiO_2	• special sites formed at the metal-support interface (Pt-TiO_x) • composed of at least one metal atom adjacent to a defect site on the support such as a Ti^{3+} cation or an oxygen vacancy. • interaction occurs between the oxygen atom of the C=O group and the support.
Yoshitake et al. (57,58)	acrolein	Ir/Nb_2O_5, Pt/Nb_2O_5, Rh/Nb_2O_5	• formation of new catalytic sites NbO_x periphery of the metal particles Two sites: • bare metal surface (hydrogen dissociation) • periphery of NbO_x islands (adsorbed acrolein and hydrogen atoms react)

TABLE 3. (continued)

Kaspar et al. (61)	crotonaldehyde	Rh/TiO_2, Ru/TiO_2, Os/TiO_2, Ir/TiO_2	• new catalytic sites • decoration of the metal particles with TiO_x
Touroude et al. (62,63)	crotonaldehyde	Pt/TiO_2	Two types of sites • hydrogenation of the C=C bond occurs on metallic sites which are poisoned in the initial stages of reaction • hydrogenation of the C=O bond (interfacial sites between the support and the metal particles, $PtTiO_x$)
Raab and Lercher (64-67)	crotonaldehyde	$PtNi/SiO_2$, $PtSn/SiO_2$, $PtGa/SiO_2$, Pt/TiO_2	• polarity at the metal surface • charge transfer when the electronegativities of the two metals are drastically different • metal ions or metal oxide particles decorating the surface of the Pt crystallites acting as strong electron pair acceptor sites for the free electron pairs of the oxygen atom of the C=O group.
Hutchings et al. (73)	crotonaldehyde	Cu/Al_2O_3 (sulfur)	• S selectively poisons the hydrogenation of the C=C bond instead of the C=O bond.
Marinelli et al. (69)	acrolein	Pt/SiO_2 Promoters: Na, Ti, V, Fe, Ga, Ge, Sn	• ensemble size effect (minor importance) • ratio in which the promoter activates the C=C bond and C=O bond is influenced by the accessibility of the olefinic bond as well as the nature of the promoting cation.

TABLE 3. (continued)

Nitta et al. (77)	crotonaldehyde cinnamaldehyde	Co/SiO_2	• Cl favorable crystalline size distribution of cobalt during hydrogen reduction by facilitating the reduction of cobalt species with metal-support interaction • chlorine hampers the C=C bond activation
Coq et al. (78)	acrolein	Ru/ZrO_2	• ensemble effect
Coq et al. (79)	acrolein methacrolein crotonaldehyde 3-methyl crotonaldehyde	Ru/Al_2O_3 promoted with Sn, Fe, Sb, Ge, Zn	• tilting of the alkyl chain far from the surface • factor is more important than activation of the carbonyl bond by electron deficient species.
Coq et al. (80)	cinnamaldehyde	Ru/Al_2O_3, RuSn/Al_2O_3, RuGe/Al_2O_3, RuZn/Al_2O_3, RuSb/Al_2O_3, RuFe/Al_2O_3, RuAg/Al_2O_3, Ru/SiO_2, Ru/G, Ru/TiO_2, Ru/ZrO_2	• addition of the second metal to Ru forces the molecule to adsorb via the carbonyl group • geometric effect • electronic effect was suggested for the RuSn/Al_2O_3 due to an increased selectivity to cinnamyl alcohol at higher conversions of cinnamaldehyde.
Coq et al. (81)	cinnamaldehyde	Ru/ZrO_2	• interfacial Ru-Zr^{n+} sites at the periphery of the particles.

Pt-Sn Bimetallic Catalysts

Catalytic reforming is a refinery process in which the principal objective is the selective conversion of saturated hydrocarbons to aromatic hydrocarbons so as to produce high octane number components for gasoline. Up until the 1970s supported monometallic catalysts were used as the primary catalyst for this process. Addition of a second metal helps in achieving better activity maintenance which is believed to be due to a change in the selectivity of coke forming reactions. Bimetallic catalysts such as Pt-Re, Pt-Ir, and Pt-Sn supported on acidified alumina have been extensively applied to the reforming process.

The general consensus among many researchers is that the main effects of the addition of tin to Pt/Al_2O_3 reforming catalysts are to enhance the selectivity for aromatization and to reduce the deactivation of the catalyst by inhibiting coke deposition. However, the role of tin and the state of tin in $Pt\text{-}Sn/Al_2O_3$ bimetallic catalysts remains a controversial issue.

Theoretical investigations of the Pt-Sn system by Van Santen (82) and Williams (83) led to the prediction that the surface of the bimetallic cluster will be strongly enriched in tin, with a corresponding depletion of tin in the layer directly below the surface. Bouwman and Biloen (84) used XPS and Auger spectroscopy and Verbeek and Sachtler (85) used TPD to examine Pt-Sn alloys and found that the experimental results they obtained were in agreement with the theories of Van Santen and Williams. Verbeek and Sachtler also found that as the proportion of tin in the alloys was increased the desorption of carbon monoxide and deuterium became much easier. This behavior was attributed to relaxing of the chemisorptive bond caused by the platinum atoms becoming surrounded by tin atoms. They referred to this as a "ligand effect".

Pt-Sn bimetallic clusters are easily formed when supported on silica (86-92). Dautzenberg et al. (86), Srinivasan and Davis (91), and Meitzner (92) found that the dispersion of the metals is higher when alumina is used as a support compared to silica. High metal dispersion is a desirable feature in reforming catalysts (92). Clearly this has an impact on the choice of support for reforming catalysts. Meitzner using EXAFS also found that the presence of tin has the effect of decreasing the number of unfilled d states associated with platinum atoms.

A variety of characterization techniques have been used in an attempt to analyze Pt-Sn/Al_2O_3 catalysts to determine the role and state of tin in the catalysts. Results using x-ray diffraction (XRD) (93-95) suggest that a Pt-Sn alloy is present in a reduced catalyst which has the composition Pt:Sn = 1:1. However, approximately 65% of the tin present in the reduced catalyst is in a form that is not detected by XRD. They suggested that the surface of the alumina consists of two parts: a surface monolayer of a tin aluminate compound and a Pt-Sn alloy. They also reported that increasing the Sn/Pt ratio increases the amount of PtSn(1:1) alloy rather than forming a mixture of alloy phases in which the tin rich alloys dominate at the higher Sn/Pt ratios. This indicates the presence of unalloyed platinum in catalysts with low loadings. Srinivasan and Davis believe that as tin is initially added to the catalyst its role is to react with the support and thereby increase the platinum dispersion. Further increases in tin concentration leads to formation of Sn(0) which forms an alloy with platinum of the composition PtSn (1:1). With further increases in tin loading the amount of tin in the zero valent state exceeds the moles of platinum and a fraction will be present as Sn(0) next to well dispersed PtSn (or even some tin rich) alloy. They also noted that the extent of the reduction and dispersion of platinum depends on the Sn/Pt ratios, surface area and the nature of the support. Dautzenberg et al. (86) also detected a PtSn alloy using XRD but only after the catalyst had been reduced in hydrogen for 100 hours at 650°C.

Temperature programmed reduction (TPR) yielded data with mixed results. Several researchers have suggested that tin is not reduced below Sn(II) on alumina based catalysts (87, 96, 97). However, Burch et al. (96) reported that the presence of platinum catalyzes the reduction of tin. The tin is believed to be strongly bonded to the alumina which may act more as a surface modifier of the support or as an electronic promoter than as an alloying component. Burch and Garla (98) have proposed that the role of tin is two-fold: tin improves the dispersion of platinum by preventing sintering of the initial very small particles and modifies the acidity of the support.

Dautzenberg et al. (86) found reduction of tin to the zero valent state and also reported the presence of Pt-Sn bimetallic clusters which are in intimate contact with each other based on results obtained from TPR studies. The supported Pt-Sn catalysts were not homogeneously alloyed, they also contained free Pt and Pt rich alloys. They claimed that the role of tin is to reduce the number of platinum surface ensembles therefore, decreasing hydrogenolysis and coke forming reactions.

Lieske and Volter (99) also used TPR experiments to examine Pt-Sn/Al_2O_3 reforming catalysts. They reported that the major part of tin was reduced to Sn(II) but a small amount of Sn(0) was also present. These results were verified by separate hydrogen and oxygen adsorption studies. They found that hydrogen adsorption decreased strongly with an increase in tin content which indicated alloy formation. A decrease in dispersion was ruled out as an explanation due to the fact that methane was adsorbed on both Pt/Al_2O_3 and Pt-Sn/Al_2O_3 to the same extent therefore, indicating the same dispersion. Oxygen adsorption was reported to increase with increasing tin content which confirms the presence of Sn(0) because Sn(II) doesn't adsorb oxygen. They also stated that the presence of platinum catalyzed the reduction of tin which agrees with Burch (96) and that the composition of the alloy only depends on the total tin content. This disagrees with the findings of Dautzenberg et al. (85) and Bacaud et al. (100) who claim that part of platinum is “free” and coexists with PtSn alloys. The role of tin suggested by

Lieske and Volter is that Sn(II) modifies the surface of alumina which causes changes in the reactivity due to an electronic reaction between platinum and Sn(II)-alumina.

X-ray photoelectron spectroscopy (XPS) studies (87,90,101) revealed that the majority of Sn is present in an oxidized form, however other XPS studies exhibited tin in the zero valent state. In the cases where no metallic Sn was detected the presence of small amounts below the detection limits was not ruled out. Adkins and Davis (101) suggested that the tin is present as an “eggshell” of tin aluminate on the alumina support with metallic platinum on top of the tin aluminate. Sexton et al. (87) and Burch (96) tried a variety of catalyst preparations but tin was not reduced below Sn(II). Balakrishnan and Schwank (90) believe that the interaction between alumina and tin inhibits the complete reduction of tin but they reported that tin was always located fairly close to the platinum particles.

Baronetti et al. (102) and Li et al. (88,103) reported the presence of Sn(0) in Pt-Sn/Al_2O_3 catalysts using XPS. Baronetti and coworkers stated that the presence of platinum is essential for reduction of tin to the zero valent state. They reported that Sn/Al_2O_3 poisons the strong acid sites of alumina. It is believed that a strong poisoning of the acidic sites would indicate a larger amount of tin stabilized on the alumina which in turn would leave a smaller amount of zero valent tin available to form alloys with platinum. They noted a lower poisoning effect of the support acidity where high alloy formation existed. Li and coworkers found that the composition of Pt-Sn alloy became richer in tin when the Pt:Sn ratio changed from 1:1 to 1:8. Also, metallic tin and presumably alloy formation occurs to a greater extent when platinum and tin are added as a complex dissolved in acetone as compared to either coprecipitation and coimpregnation.

Mössbauer spectroscopy is another technique which has been used to characterize supported Pt-Sn bimetallic catalysts. Mössbauer spectroscopy can distinguish between Sn(II) and Sn(IV) and it can supply direct evidence of alloy formation. However, it is difficult to assess the presence of Sn(II) or whether Sn(0) is alloyed with platinum. Bacaud et al. (100) and Kuznetsov et al. (104) found large amounts of Pt-Sn alloys, Sn(IV) and Sn(II) ionic species and rather large amounts of free Pt in Pt-Sn/Al_2O_3 catalysts using Mössbauer. Bacaud et al. (100) reported that a decrease in catalytic activity in the conversion of n-heptane over Pt-Sn/Al_2O_3 compared to Pt/Al_2O_3 was due to alloy formation. They also stated that tin ions could be responsible for poisoning the strong acidic sites of alumina. Li et al. (89) used Mössbauer spectroscopy along with XRD to investigate Pt-Sn/Al_2O_3 and Pt-Sn/SiO_2 catalysts. The only significant alloy phase detected was PtSn (1:1) along with oxidized forms of tin. They also found a form of tin that had a very different environment than tin in a pure metal. They suggested that tin is retained in the small pores of the silica and that there is a strong interaction between the tin and the support. The tin metal atoms could possibly donate electrons to the support. Li et. al (89) reported that the fraction of platinum present in an alloy phase is dependent on the tin concentration and approached 100% alloy formation for Sn:Pt ratios greater than five.

Adsorption of gases on Pt-Sn/Al_2O_3 catalysts is another method many researchers have used to characterize the surface of Pt-Sn/Al_2O_3 catalysts. There are contradictory results reported in literature concerning the effect of tin on the adsorption of hydrogen on Pt-Sn/Al_2O_3. Burch (96) and Muller et al. (97) reported an increase in the amount of hydrogen chemisorbed by platinum when tin is present. Burch attributed this to an increase in platinum dispersion by suppressing the sintering of the platinum particles. Muller et al. (97) speculated that hydrogen was being retained by Sn(II) ions on the surface of the alumina which could account for the increase in the amount of hydrogen adsorbed. Several other authors (85, 99, 105) reported a decrease in the amount of hydrogen adsorbed on platinum with an increasing tin content. Since dissociative adsorption of hydrogen is likely to require two platinum atoms which may need to be adjacent Verbeek and Sachtler (85) suggested that the introduction of a tin atom between the two platinum atoms might make dissociative adsorption an activated process. Another possible explanation given was the presence of a strong ligand effect which would result in a dramatic lowering of the heat of adsorption of hydrogen on the platinum atoms of the alloy surface. Lieske and Volter (99) attributed the decrease in hydrogen adsorption to the formation of alloys. A decrease in platinum dispersion was ruled out in a separate experiment where methane was adsorbed in equal amounts on both Pt/Al_2O_3 and Pt-Sn/Al_2O_3 which was also verified by XRD data. They also claim that hydrogen adsorption is not a accurate measure for the dispersion of Pt-Sn/Al_2O_3 because tin can decrease (0°C) or even slightly increase (300°C) hydrogen adsorption depending on the temperature of adsorption. Balakrishnan and Schwank (90) observed an increase in the hydrogen uptake when small amounts of tin were added but further additions of tin caused a decrease in the amount of hydrogen adsorbed. The larger hydrogen uptake found on the low loading bimetallics compared to Pt/Al_2O_3 was attributed to a higher platinum dispersion bimetallics. The decrease in hydrogen uptake with increasing tin content was suggested to be due to tin enrichment at the surface atoms of the catalyst thereby covering the platinum surface but XPS results did not support this speculation. Another reason given was that the Sn(II) ions become firmly attached to the alumina support with Pt atoms dispersed among the tin aluminate complex. The distance between the platinum atoms would increase with additions of tin which would decrease the number of platinum ensembles capable of hydrogen dissociation. Also, another possibility is that some platinum atoms could be covered by the tin-alumina matrix and therefore, become inaccessible for adsorption of gases.

Balakrishnan and Schwank (90) also investigated carbon monoxide and oxygen adsorption on Pt-Sn/Al_2O_3 catalysts. Similar adsorption behavior was reported for hydrogen and carbon monoxide. However, compared to hydrogen, carbon monoxide seemed to be less sensitive to the platinum ensemble size and may represent a more simple probe molecule for counting the accurate number of platinum surface atoms in Pt-Sn/Al_2O_3 as long as the system doesn't display any chemisorption induced surface segregation effects. They observed no significant change in the amount of weakly adsorbed hydrogen after the addition of approximately 50 at.% tin and upon further additions of tin, therefore they believe that the Pt-H and Pt-CO bonds were not significantly weakened upon addition of Sn to Pt/Al_2O_3. They found a steady increase in gas uptake with increasing tin content for the adsorption of oxygen. This would indicate the presence of Sn(0) since Sn(II) doesn't adsorb oxygen which agrees with results from Lieske and Volter (99). However, XPS data did not reveal the presence of Sn(0). Another possible reason for the increase in oxygen uptake is that the chemisorption stoichiometry of oxygen adsorption on surface platinum atoms may become modified by the presence of tin. The strength of the Pt-O bond was not influenced by tin addition and oxygen is much more strongly held than hydrogen at room temperature.

Gebhard et al. (106) studied hydrogen adsorption on ordered Sn/Pt(111) surface alloys. They found a large inhibition of hydrogen adsorption which is due to a substantial increase in the activation energy for dissociative adsorption of hydrogen on the alloy surface compared to Pt(111). This could be caused by the physical removal of or the electronic modification of the most reactive ensemble of contiguous platinum atoms necessary for hydrogen dissociation on Pt(111). Modification of the platinum atom electronic structure by alloying with tin could also increase the activation energy for hydrogen adsorption and inhibit hydrogen dissociation. Theoretical calculations by Harris and Anderson (107) for hydrogen dissociation on metals suggest that increasing the d-electron density on platinum will increase the activation energy for hydrogen adsorption and inhibit hydrogen dissociation. They also found that tin atoms do not simply block hydrogen adsorption sites in the Pt(111) surface.

Gebhard and coworkers (106) also investigated the chemisorption of carbon monoxide on Sn/Pt(111) surface alloys. They reported a slight weakening of the carbon monoxide chemisorption bond on the alloys which agrees with adsorption data of Verbeek and Sachtler (85). Work involving coadsorption of carbon monoxide with other electron donors, e.g., alkali metals demonstrated a strengthening of the surface-CO bond which is in contrast with the above mentioned reduction in the desorption energy.

References

1. Blue, E. M. Hydrocarbon Process 1969, **48**(9), 141.
2. Beltramini, J.; Trimm, D. L. Appl. Catal. 1983, **32**, 149.
3. Clippinger, E.; Muslakey, B. F. U. S. Patent 353143, 1970.
4. Satterfield, C. N. Heterogeneous Catalysis in Practice; McGraw-Hill, 1980.

5. Allmang, G.; Grass, F.; Grosselin, J. M.; Mercier, C. J. Molec. Catal. 1991, **66**, L27.

6. Pak, A. M.; Konuspaev, S. R.; Zakumbaeva, G. D.; Sokolskii, D. V. React. Kinet. Catal. Lett. 1981, **16**, 339.

7. Seo, G.; Chon, H. J. Catal. 1981, **67**, 424.

8. Rylander, P. N. Catalytic Hydrogenation in Organic Syntheses; Academic Press: New York, 1979.

9. Rylander, P. Catalytic Hydrogenation over Platinum Metals; Academic Press: New York and London, 1967.

10. Lau, C. P.; Ren, C. Y.; Chu, M. T.; Yeung, C. H. J. Molec. Catal. 1991, **65**, 287.

11. Tuley, W. F.; Adams, R. J. Am. Chem. Soc. 1925, **47**, 3061.

12. Rylander, P. N.; Himelstein, N.; Kilroy, M. Engelhard Ind. Tech. Bull. 1963, 4, 49.

13. Rylander, P. N.; Himelstein, N. Engelhard Ind. Tech. Bull. 1964, **4**, 131.

14. Rylander, P. N.; Steele, D. R. Tetrahedron Lett. 1969, 1579.

15. Khidekel, M. L.; Bakhanova, E. N.; Astakhova, A. S.; Brikenshtein, K. A.; Savchenko, V. I.; Manakhova, I. S.; Dorokhov, V. G. Izv. Akad. Nauk SSSR, Ser. Khim. 1970, 499.

16. Steiner, K. U. S. Patent 3,953,524, Apr. 27, 1976.

17. Ichikawa, Y.; Suzuki, M.; Sawaki, T. Jpn. Patent 77 84,193, July 13, 1977; Chem. Abstr. 1977a, **87**, 200794v.

18. Ichikawa, Y.; Yamaji, T.; Sawaki, T. Jpn. Patent 77 46,008, Apr. 12, 1977; Chem. Abstr. 1977b, **87**, 136052x.

19. Ichikawa, Y.; Teizo, Y. Jpn. Patent 77 12,106, Jan. 29, 1977; Chem. Abstr. 1977, **87**, 52778a.

20. Vanderspurt, T. H. U. S. Patent 4,048,110, Sept. 12, 1977a.

21. Vanderspurt, T. H. U. S. Patent 4,020,116, Apr.26, 1977b.

22. Jenck, J.; Germain, J. J. Catal. 1980, **65**, 141.

23. Hubaut, R.; Daage, M.; Bonnelle, J. P. Appl. Catal. 1986, **22**, 231.

24. Hubaut, R.; Daage, M.; Bonnelle, J. P. Stud. Surf. Sci. Catal. 1988, **41**, 131.

25. Sokolskii, D. V.; Zharmagambetova, A. K.; Anisimova, N. V. React. Kinet. Catal. Lett. 1986, **30**(1), 101.

26. Sokolskii, D. V.; Anisimova, N. V.; Zharmagambetova, A. K. Dokl. Akad. Nauk SSSR 1979, **249**, 139.

27. Sokolskii, D. V.; Anisimova, N. V.; Zharmagambetova, A. K. Bull. Izobret. 1981, **6**.

28. Sokolskii, D. V.; Anisimova, N. V.; Zharmagambetova, A. K.; Mukhamedzhanova, S. G.; Edygenova, L. N. React. Kinet. Catal. Lett. 1987, **33**(2), 399.

29. Galvagno, S.; Staiti, P.; Antonucci, P.; Donato, A.; Peitropaolo, R. J. Chem. Soc. Faraday Trans. 1 1983, **79**, 2605.

30. Galvagno, S.; Poltarzewski, Z.; Donato, A.; Neri, G.; Pietropaolo, R. J. Molec. Catal. 1986, **35**, 365.

31. Poltarzewski, Z.; Galvagno, S.; Pietropaolo, R.; Staiti, P. J. Catal. 1986, **102**, 190.

32. Galvagno, S.; Poltarzewski, Z.; Donato, A.; Neri, G.; Pietropaolo, R. J. Chem. Soc. Chem. Commun. 1986, 1729.

33. Galvagno, S.; Donato, A.; Neri, G.; Pietropaolo, R.; Pietropaolo, D. J. Molec. Catal. 1989, **49**, 223.

34. Galvagno, S.; Capannelli, G.; Neri, G.; Donato, A.; Pietropaolo, R. J. Molec. Catal. 1991, **64**, 237.

35. Galvagno, S.; Donato, A.; Neri, G.; Pietropaolo, R. Catal. Lett. 1991, **8**, 9.

36. Galvagno, S.; Milone, C.; Donato, A.; Neri, G.; Pietropaolo, R. Catal. Lett. 1993, **18**, 349.

37. Galvagno, S.; Donato, A.; Neri, G.; Pietropaolo, R.; Capannelli, G. J. Molec. Catal. 1993, **78**, 227.

38. Goupil, D.; Fouillox, F.; Maurel, R. React. Kinet. Catal. Lett. 1987, **35**, 185.

39. Goupil, D. Ph. D. dissertation, University of Lyon, 1986.

40. Richard, D.; Fouillox, P.; Gallezot, P. Proc. 9th Int. Congr. on Catalysis, 1988, **3**, 1074.

41. Giroir-Fendler, A.; Richard, D.; Gallezot, P. Stud. Surf. Sci. Catal. 1988, **41**, 171.

42. Richard, D.; Ockelford, J.; Giroir-Fendler, A.; Gallezot, P. Catal. Lett. 1989, **3**, 53.
43. Gallezot, P.; Giroir-Fendler, A.; Richard, D. Catal. Lett. 1990, **5**, 169.
44. Giroir-Fendler, A.; Richard, D.; Gallezot, P. Catal. Lett. 1990, **5**, 175.
45. Nitta, Y.; Ueno, K.; Imanaka, T. Appl. Catal. 1989, **56**, 57.
46. Blackmond, D. G.; Waghray, A.; Oukaci, R.; Blanc, B.; Gallezot, P. Stud. Surf. Sci. Catal. 1990, **59**, 145.
47. Blackmond, D. G.; Oukaci, R.; Blanc, B.; Gallezot, P. J. Catal. 1991, **131**, 401.
48. Simonek, J.; Beranek, P. Collect. Czech. Commun. 1972, **37**, 353.
49. Waghray, A.; Oukaci, R.; Blackmond, D. G. Stud. Surf. Sci. Catal. 1992, **75**, 2479.
50. Waghray, A.; Wang, J.; Oukaci, R.; Blackmond, D. G. J. Phys. Chem. 1992, **96**, 5954.
51. Blackmond, D. G.; Waghray, A. Catalysis of Organic Reactions; Marcel Dekker: New York, 1995.
52. Waghray, A.; Blackmond, D. G. J. Phys. Chem. 1993, **97**, 6002.
53. van Hardeveld, R.; Hartog, F. Adv. Catal. 1975, **22**, 75.
54. Vannice, M. A.; Sen, B. J. Catal. 1989, **115**, 65.
55. Vannice, M. A. J. Molec. Catal. 1990, **59**, 165.
56. Vannice, M. A. Catal. Today 1992, **12**, 255.

57. Yoshitake, H.; Asakura, K.; Iwasawa, Y. J. Chem. Soc. Faraday Trans. 1 1989, **85**(8), 2021.

58. Yoshitake, H.; Iwasawa, Y. J. Catal. 1990, **185**, 227.

59. Wismeijer, A. A.; Kieboom, A. P. G.; van Bekkum, H. React. Kinet. Catal. Lett. 1985, **29**(2), 311.

60. Wismeijer, A. A.; Kieboom, A. P. G.; van Bekkum, H. Appl. Catal. 1986, **25**, 181.

61. Kaspar, J.; Gaziani, M.; Escobar, G. P.; Trovarelli, A. J. Molec. Catal. 1992, **72**, 243.

62. Touroude, R. J. Catal. 1980, **65**, 110.

63. Makouangou-Mandilou, R.; Touroude, R.; Dauscher, A. Stud. Surf. Sci. Catal. 1993, **78**, 219.

64. Raab, C. G.; Lercher, J. A. J. Molec. Catal. 1992, **75**, 71.

65. Raab, C. G.; Englisch, M.; Marinelli, T. B. L. W.; Lercher, J. A. Stud. Surf. Sci. Catal. 1993, **78**, 211.

66. Jentys, A.; Raab, C. G.; Lercher, J. A. Stud. Surf. Sci. Catal. 1992, **75**, 2301.

67. Raab, C. G.; Lercher, J. A. Catal. Lett. 1993, **18**, 99.

68. Jentys, A.; McHugh, B.; Haller, G. L.; Lercher, J. A. J. Phys. Chem. 1992, **96**, 1324.

69. Marinelli, T. B. L. W.; Vleeming, J. H.; Ponec, V. Stud. Surf. Sci. Catal. 1992, **75**, 1211.

70. Marinelli, T. B. L. W.; Nabuurs, S.; Ponec, V. J. Catal. 1995, **151**, 431.

71. Merta, R.; Ponec, V. Proc. 4th Intern. Congress on Catalysis, 1968, **2**, 53.

72. Affrossman, S.; Cvetanovic, R. J. Canad. J. Chem. 1964, **45**, 1206.

73. Hutchings, G. J.; King, F.; Okoye, I. P.; Rochester, C. H. Appl. Catal. 1992, **83**, L7.

74. Ponec, V. Catal. Today 1992, **12**, 227.

75. Beccat, P.; Bertolini, J. C.; Gauthier, Y.; Mussardier, J.; Ruiz, P. J. Catal. 1990, **126**, 451.

76. Noller, H.; Lin, W. M. J. Catal. 1984, **85**, 25.

77. Nitta, Y.; Hiramatsu, Y.; Imanana, T. J. Catal. 1990, **126**, 235.

78. Coq, B.; Figueras, F.; Geneste, P.; Moreau, C.; Moreau, P.; Warawdekar, M. J. Molec. Catal. 1993, **78**, 211.

79. Coq, B.; Figueras, F.; Moreau, C.; Moreau, P.; Warawdekar, M. Catal. Lett. 1993, **22**, 189.

80. Coq, B.; Kumbhar, P. S.; Moreau, C.; Moreau, P.; Warawdekar, M. G. J. Molec. Catal. 1993, **85**, 215.

81. Coq, B.; Kumbhar, P. S.; Moreau, C.; Moreau, P.; Figueras, F. J. Phys. Chem. 1994, **98**, 10180.

82. Van Santen, R. A.; Sachtler, W. M. H. J. Catal. 1974, **33**, 202.

83. Williams, F. L.; Boudart, M. J. Catal. 1973, **30**, 438.

84. Bouwman, R.; Biloen, P. Surf. Sci. 1974, **41**, 348.

85. Verbeek, H.; Sachtler, W. M. H. J. Catal. 1976, **42**, 257.

86. Dautzenber, F. M.; Helle, J. N.; Biloen, P.; Sachtler, W. M. H. J. Catal. 1980, **63**, 119.

87. Sexton, B. A.; Hughes, A. E.; Foger, K. J. Catal. 1984, **88**, 466.

88. Li, Y.; Stencel, J. M.; Davis, B. H. Appl. Catal. 1990, **64**, 71.

89. Li, Y.; Klabunde, K. J.; Davis, B. H. J. Catal. 1991, **128**, 1.

90. Balakrishnan, K.; Schwank, J. J. Catal. 1991, **127**, 287.

91. Srinivasan, R.; Davis, B. H. Appl. Catal. 1992, **87**, 45.

92. Meitzner, G.; Via, G. H.; Lytle, F. W.; Fung, S. C.; Sinfelt, J. H. J. Phys. Chem. 1988, **92**, 2925.

93. Srinivasan, R.; De Angelis, R. J.; Davis, B. H. J. Catal. 1987, **106**, 449.

94. Srinivasan, R.; De Angelis, R. J.; Davis, B. H. Catal. Lett. 1990, **4**, 303.

95. Srinivasan, R.; Rice, L. A.; Davis, B. H. J. Catal. 1991, **129**, 257.

96. Burch, R. J. Catal. 1981, **71**, 348.

97. Muller, A. C.; Engelhard, P. A.; Weisang, J. E. J. Catal. 1979, **56**, 65.

98. Burch, R.; Garla, L. C. J. Catal. 1981, **71**, 360.

99. Lieske, H.; Volter, J. J. Catal. 1984, **90**, 96.

100. Bacaud, R.; Bussiere, P.; Figueras, F. J. Catal. 1981, **69**, 399.

101. Adkins, S. R.; Davis, B. H. J. Catal. 1984, **89**, 371.

102. Baronetti, G. T.; de Miguel, S. R.; Scelza, O. A.; Castro, A. A. Appl. Catal. 1986, **24**, 109.

103. Li, Y.; Stencel, J. M.; Davis, B. H. . React. Kinet. Catal. Lett. 1988, **37**(2), 273.

104. Kuznetsov, V. I.; Belyi, A. S.; Yurchenko, E. N.; Smolikov, M. D.; Protasova, R. T.; Zatolokina, E. V.; Duplyakin, V. K. J. Catal. 1986, **99**, 159.

105. Volter, J.; Lietz, G.; Uhlemann, M.; Hermann, M. J. Catal. 1981, **68**, 42.

106. Gebhard, S. C.; Windham, R. G.; Koel, B. J. Phys. Chem. 1990, **94**, 6831.

107. Harris, J.; Andersson, S. Phys. Rev. Lett. 1985, **55**, 1583.

108. Uner, D. O.; Pruski, M; King; T. S. submitted for publication.

109. Smale, M. W.; King, T. S. J. Catal. 1989, **119**, 441.

110. Strohl, J. K.; King, T. S. J. Catal. 1989, **116**, 540.

CONCLUSIONS

A number of conclusions can be drawn from the work discussed in this dissertation:

1. The hydrogenation of crotonaldehyde over Pt/SiO_2 produced only butyraldehyde and was less active than the hydrogenation of crotonaldehyde over $Pt\text{-}Sn/SiO_2$.
2. Crotonaldehyde was selectively hydrogenated to crotyl alcohol over $Pt\text{-}Sn/SiO_2$ catalysts.
3. The method of catalyst preparation for $Pt\text{-}Sn/SiO_2$ catalysts affected the selectivity to crotyl alcohol. The most selective Pt-Sn catalysts were those in which the Sn precursor was dissolved in a HCl solution.
4. Sn increased both the rate of formation of butyraldehyde and the rate of formation of crotyl alcohol in the hydrogenation of crotonaldehyde.
5. The presence of Sn increased the H/Surface Pt ratio. That is, Sn promotes additional hydrogen adsorption per surface Pt atom. This additional hydrogen is more weakly bound.
6. Initial heats of adsorption (~ 90 kJ/mol) measured using microcalorimetry were not affected by the presence of Sn on Pt. We can conclude that there is no through metal electronic interaction between Pt and Sn at least with respect to hydrogen surface bonds since Pt and Pt-Sn had similar initial heats of adsorption coupled with the invariance of the ^1H NMR Knight shift.

7. The hydrogenation of crotonaldehyde carried out over Pt-Ag/SiO_2 and Pt-Cu/SiO_2 bimetallic catalysts produced 100% butyraldehyde.
8. Selective site blocking of low coordination edge, corner and other defect-like sites by Cu or Ag as well as reduction in the Pt ensemble size did not lead to the formation of crotyl alcohol as has been postulated in previous work.
9. These low coordination edge and corner sites cannot be responsible for the olefin hydrogenation activity since the TOF for Pt-Ag/SiO_2 and Pt/SiO_2 were identical.
10. The presence of additional adsorbed hydrogen on both Pt-Sn and Pt-Cu is correlated with the increased activity obtained for these catalyst systems relative to pure Pt and Pt-Ag.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to Dr. Terry King for his encouragement and guidance throughout my stay at Iowa State University. I would also like to thank Dr. Doraiswamy for his valuable comments and suggestions for this research project. A special thanks is due to all the students in Dr. King's research group and to all others who have made my stay here in Ames enjoyable. It has been a great experience!

This work was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1779 to this dissertation.