

## Vapor-Phase Aldol Condensation of *n*-Butyraldehyde Using a Reduced Tin-Silica Catalyst

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Tin oxide supported on silica gel can be activated to form an active catalyst for the aldol condensation of *n*-butyraldehyde to 2-ethyl-hexenal. The activation involves reducing the tin with hydrogen. The reaction can be carried out continuously with no catalyst aging providing that a hydrogen: butyraldehyde mole ratio of over five is used. At lower ratios the aldehyde slowly oxidizes the tin to an inactive state. Ammonia adsorption measurements suggest that the high activity of the reduced catalyst is due to an increase in surface acidity. However, the possibility of a direct reaction of butyraldehyde with tin is discussed. Studies of catalyst reducibility and the state of tin were made.

### INTRODUCTION

In recent years there have been several publications on vapor-phase aldol condensation reactions using solid catalysts. Malinowski and co-workers (1, 2) made extensive studies on the aldol condensation reactions of formaldehyde with other aliphatic aldehydes using treated silica catalysts. Czarny (3) found that crotonaldehyde was produced when acetaldehyde and water vapor were passed over a treated silica-tantalum oxalate catalyst at 300°C. Scheidt (4) reported the use of lithium phosphate for catalyzing various condensation reactions. A recently issued patent (5) described the vapor-phase condensation of *n*-butyraldehyde over a zinc oxide-molybdena catalyst. Acrylic acid has been prepared by an aldol-type reaction between acetic acid and formaldehyde using various solid catalysts (6). The use of zeolites for various condensation reactions has also been reported (7).

We report on a catalyst system consisting of tin supported on silica gel which catalyzes the aldol condensation of *n*-butyraldehyde to 2-ethyl-hexenal (ethyl propyl acrolein) at very high selectivities. From this study, it has been found that the state of the tin

is very important in order to obtain high conversions and selectivities with long catalyst life. This reaction is of considerable importance since the 2-ethyl-hexenal can be hydrogenated to 2-ethyl-hexanol which finds extensive use as a plasticizer component.

### EXPERIMENTAL METHODS

#### *Catalyst Preparation*

The main catalyst used in this study was prepared by impregnating Davison Grade 70 silica gel (260 m<sup>2</sup>/g) to the point of incipient wetness with aqueous stannous chloride. Upon addition of stannous chloride to water, a white precipitate formed, probably a hydrated stannous oxychloride. A suspension of the precipitate was then dispersed on the silica gel. In addition, a chloride-free catalyst was prepared by dissolving tin metal in 6 *N* nitric acid, diluting with water, and dispersing the white solid on the silica gel. Both catalysts were dried at 110°C for approximately 16 hr and then calcined for 16 hr at 500°C. All tests were made on the chloride-prepared catalyst containing 10 wt % tin unless otherwise stated.

### *Catalyst Characterization*

Catalyst surface areas were determined by the standard BET method using nitrogen as the absorbate. Surface acidity was obtained using ammonia gas adsorption method of Barth and Bellou (8). X-Ray diffraction patterns of the catalysts were obtained with a Norelco diffractometer using nickel-filtered  $\text{CuK}\alpha$  radiation.

Catalyst reduction studies were made in a flowing stream at atmospheric pressure, using a Cahn electrobalance to monitor weight loss attending reduction. The catalyst (200 mg), contained in a quartz bucket, was first heated to reaction temperature in a nitrogen flow and held at temperature until no further water loss ensued (1–2 hr). Then a hydrogen flow was introduced and weight changes were recorded until no further appreciable change was obtained. Reduction was generally continued overnight to establish the total reducibility of the sample. In some cases, the samples were reoxidized by purging the system with nitrogen, followed by air. The fraction converted to metal was calculated using the final reduction weight for each sample. Although the fractional conversions were consistent between samples of the same catalyst, the total amounts of reduction obtained varied somewhat ( $\pm 15\%$  from the average), indicating some sample inhomogeneity in tin content. This is not

catalyst bed. The temperature of the furnace was controlled with a variac in conjunction with a Foxboro model 4036 potentiometer controller. The parts of the reactor which were out of the furnace were wrapped with heating tape and were kept at a temperature sufficient to keep the products in the vapor phase until they reached the collection system. In all cases, 6 g of catalyst was used. The *n*-butyraldehyde was obtained from the Eastman Chemical Company and was distilled before use. The butyraldehyde was introduced into the system by means of a constant-drive syringe infusion pump (Harvard Apparatus Company model 600-000) and was vaporized in a flash zone before being carried over the catalyst in a stream of hydrogen. The hydrogen flow rate was approximately 40 ml/min in most experiments. Condensable components in the effluent were trapped out in a spiral trap immersed in a wet-ice bath.

Quantitative analyses of the organic condensate were obtained using an Aero-graph model 200 chromatograph with a 1/4 in. o.d. column, 20-ft long, packed with 10% FFAP on 20/60 mesh chromosorb W. The column temperature was programmed from 50 to 200°C at a rate of 6°C/min. Peak areas were obtained with a disc integrator.

Conversion and selectivity were determined as follows:

$$\% \text{ conversion} = 100 \times \frac{\text{moles of butyraldehyde converted}}{\text{total moles of butyraldehyde charged}}$$

$$\% \text{ selectivity} = \frac{\% \text{ conversion to 2-ethyl hexenal}}{\% \text{ total conversion}}$$

surprising in view of the preparation method used for this catalyst.

### *Reactor System*

Catalysts were tested using a laboratory-scale reactor constructed of 16 mm i.d. Pyrex glass tubing, 50 cm long, with a porous glass disc positioned midway in the reactor as a support for the catalyst bed. A thermowell was positioned in the middle of the reactor and ran the length of the

## RESULTS

### *Catalyst Studies*

The addition of tin to silica does not have a marked effect on the surface area nor does the pretreatment of the catalyst with hydrogen at 375°C over a 8-hr period. The standard calcined catalyst had a chloride content of 0.15 wt %, which decreased to 0.09% after hydrogen pretreatment. Examination of the calcined catalyst

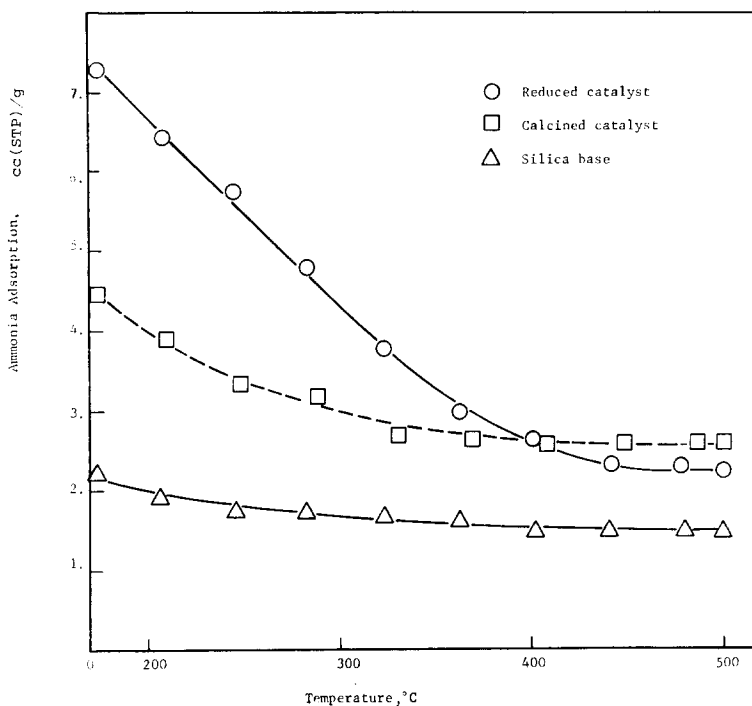


FIG. 1. Ammonia absorption at various temperatures.

by X-ray diffraction showed the presence of stannic oxide,  $\text{SnO}_2$ . After an 8-hr hydrogen treatment at  $375^\circ\text{C}$ , only  $\beta\text{-Sn}$  was observed. At shorter reduction times, the catalysts contained mixtures of  $\text{SnO}_2$  and  $\beta\text{-Sn}$ .

Ammonia gas adsorption measurements were made on three samples: the silica gel used as the catalyst support, the calcined catalyst, and the calcined catalyst which had been reduced with hydrogen at  $375^\circ\text{C}$  and atmospheric pressure for 5 hr. The latter was reduced in the adsorption cell to avoid exposure to air before ammonia adsorption measurements. The data obtained are shown in Fig. 1. The adsorption of ammonia on silica gel is very low, indicating a low surface acidity (8). The calcined catalyst adsorbs more ammonia than the base silica over the entire temperature range. The reduced catalyst adsorbs the most ammonia per gram of material at the lower part of the temperature range, indicating a greater number of weak acid sites, although the strong sites are about the same. Of particular interest is a comparison of the

amounts of ammonia adsorbed at  $250^\circ\text{C}$ , the temperature at which the catalytic measurements were carried out; the reduced catalyst adsorbs about 50% more than the calcined catalyst and about three times more than the support alone.

Reduction-oxidation cycles at  $500^\circ\text{C}$  on the calcined catalyst revealed the following changes: in hydrogen, reduction of the  $\text{SnO}_2$  to Sn occurred completely within 1 hr; reoxidation of the reduced catalyst in air was very rapid but incomplete; subsequent reduction returned the catalyst to its former reduced state; again, reoxidation was rapid and incomplete. It is probable that some coalescence of tin occurs during reduction, since tin is liquid above  $232^\circ\text{C}$ . The larger tin agglomerates show a resistance to complete oxidation, but not reduction, presumably due to diffusional phenomena, i.e., oxygen must diffuse through a tin oxide layer to react with the tin metal in oxidation; whereas hydrogen has an easy access to the tin oxide layer through a molten tin layer in reduction.

The rate of reduction of the catalyst at

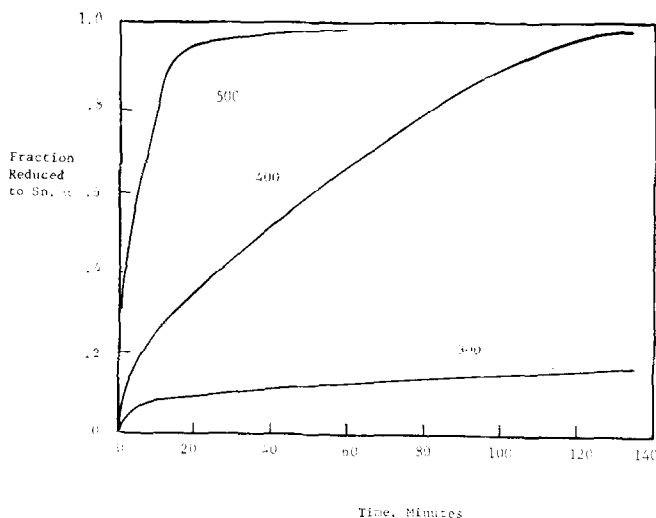


FIG. 2. H<sub>2</sub> reduction of Sn/SiO<sub>2</sub> catalyst.

several temperatures is shown in Fig. 2. The course of the reduction appears to proceed through three regimes: a rapid initial reaction, a slower, almost linear region, and a slow final region. It was not possible to fit the reduction curves to any simple gas-solid rate expressions (9).

Recourse was made to a generalized analysis to obtain activation energies for reduction. This involved evaluating the effect of temperature at several stages of conversion. Assuming that the rate of conversion is a function only of the degree of conversion,  $f(\alpha)$ , and the temperature,  $T$  (for constant pressure conditions), in any conversion stage small enough, an average rate constant,  $k$ , would apply. Thus,

$$d\alpha/dt = k(\alpha, T) \cdot f(\alpha), \quad (1)$$

where  $d\alpha/dt$  is the rate of conversion at time  $t$ . If the reaction rate is a normally activated process, the rate constant can be expressed by the Arrhenius relationship.

$$k = Ae^{-\Delta E/RT}, \quad (2)$$

where  $A$  is the frequency factor,  $\Delta E$  the activation energy for the reduction process, and  $R$  is the gas constant. Now, in a given conversion region ( $\alpha_i - \delta_i$ ) to ( $\alpha_i + \delta_i$ ), Eq. (1) becomes,

$$d\alpha/dt = A_i e^{-\Delta E_i/RT} \cdot f(\alpha). \quad (3)$$

Integration of Eq. (3) within the conversion limits yields,

$$\log \Delta t_i = \frac{\Delta E_i}{2.303RT} - \log \frac{A_i}{F(\alpha_i, \delta_i)}, \quad (4)$$

where:

$$\Delta t_i = t_{\alpha_i + \delta_i} - t_{\alpha_i - \delta_i},$$

$$F(\alpha, \delta_i) = \int_{\alpha_i - \delta_i}^{\alpha_i + \delta_i} \frac{d\alpha}{f(\alpha)}.$$

Hence, a plot of  $\log \Delta t_i$  against  $1/T$  should allow calculation of the activation energy in the given region. Such a plot is shown in Fig. 3 for five conversion regions. The respective activation energies, calculated by least squares analysis, are tabulated in Table 1. There is a very gradual drop in

TABLE 1  
ACTIVATION ENERGIES FOR REDUCTION  
OF TIN CATALYST

"Range" of conversion, $\alpha$	Activation energy (kcal/mole)
0-0.25	25
0.25-0.50	25
0.50-0.75	20
0.75-0.90	18
0.90-0.95	7

activation energy with conversion up to about 90% converted, after which the activation energy falls sharply. The change in activation energy with conversion confirms that the reduction cannot be expressed by a

simple kinetic form. Diffusional processes and retardation by product water formed probably contribute to the complex nature of the reduction. In fact, the presence of 3 mole % water in the hydrogen stream greatly retarded the rate of reduction at 425°C. The reverse reaction, oxidation of a fully reduced catalyst with a 3% H<sub>2</sub>O/N<sub>2</sub> stream, did not occur at 500°C, showing the rate of the reverse reaction to be very slow.

To check if butyraldehyde can readily oxidize the reduced tin catalyst, a completely reduced sample was reacted at 260°C with a H<sub>2</sub> stream which was saturated with aldehyde held at ice temperature (H<sub>2</sub>/butyraldehyde  $\cong$  20/1). An immediate and rapid weight gain ensued, which in 2 hr leveled out at a weight equivalent of about one-half of the fully oxidized sample. X-Ray analysis detected only metallic tin.

Therefore, if the reduced tin were oxidized by the aldehyde at this temperature, either the tin oxide phase is amorphous to X-rays or the extent of oxide formation is too small to be detected. Carbon analysis of the sample gave 0.8% C by weight, which in conjunction with the weight gain leads to the following possibilities: (i) For no tin oxidation, the residue composition is close to that for ethyl hexenal, which as an adsorbed monolayer would represent about 15% surface coverage of the silica (assuming negligible surface area for the tin); (ii) For no tin oxidation, a mixture of adsorbed butyraldehyde and coke; and (iii) For tin oxidation, the maximum extent of oxidation would be about 6% to SnO<sub>2</sub> or 12% SnO, assuming a coke composition of CH. This extent of oxidation would not be detected by X-ray analysis. Neither the silica sup-

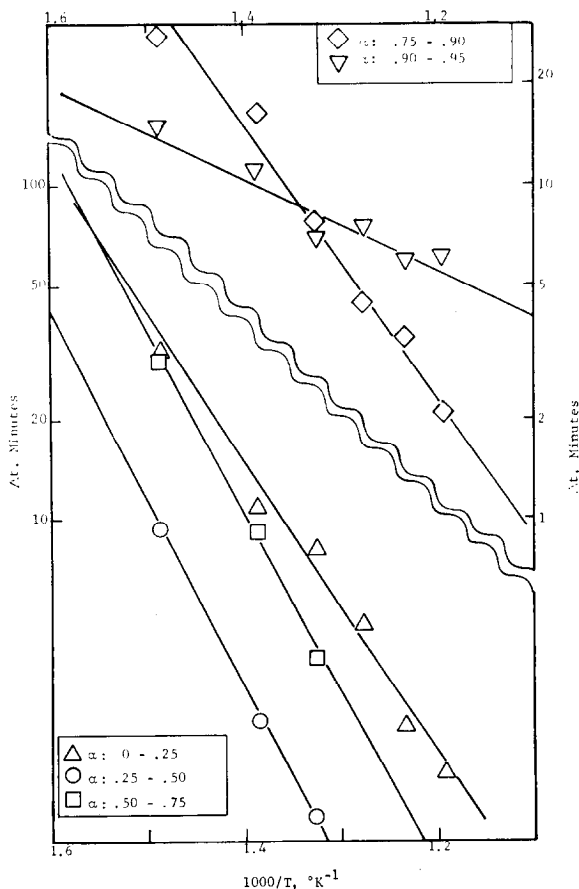


Fig. 3. Activation energy plot for reduction of Sn/SiO<sub>2</sub> catalyst: 1000/T (°K<sup>-1</sup>).

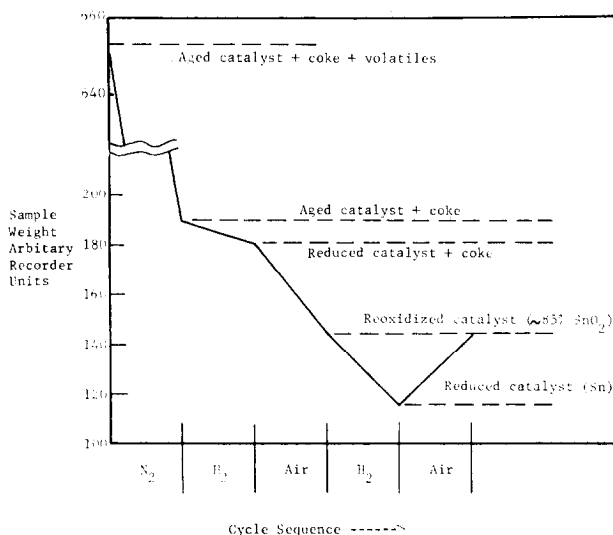


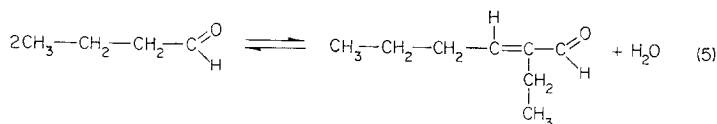
FIG. 4. Microbalance run on aged catalyst; temp. = 560°C.

port alone nor the calcined catalyst (oxidized state) gave any appreciable weight gain in a butyraldehyde/ $N_2$  stream under comparable conditions. Therefore, it is the reduced tin state that is the active species for butyraldehyde adsorption. A repeat run with the reduced tin catalyst using a butyraldehyde/ $N_2$  mixture at 400°C for 6 hr resulted in considerable coke deposition (6 wt % C). Analysis of this sample by X-ray diffraction revealed the absence of any lines over the broad silica base pattern; evidently, the tin had become amorphous to X-rays. The extent of oxidation of the tin was estimated to be 10–20% to  $SnO_2$  or 20–40% to  $SnO$  by the method outlined in the following paragraph. It seems noteworthy that  $SnO$  was never detected by X-ray analysis in any of our samples. An amorphous  $SnO$  phase may be a precursor to the slow formation of crystalline  $SnO_2$  over a period of time.

showed the presence of  $SnO_2$ . To determine the extent of oxidation of the tin in the aged catalyst, it was subjected to the following microbalance run, the results of which are shown in Fig. 4. The sample was heated in  $N_2$  to 560°C and held until no further weight loss occurred due to vaporization of volatile coke and water. Hydrogen was admitted and a weight loss occurred. Then air was introduced, burning off the coke and oxidizing the Sn to  $SnO_2$ . Finally, the sample was again subjected to a  $H_2$  reduction. From the first weight loss in  $H_2$  and the second (corrected for assumed incomplete reoxidation), the percentage of  $SnO_2$  in the aged catalyst was estimated to be 30%.

#### Reaction Studies

The aldol condensation of *n*-butyraldehyde gives 2-ethyl-hexenal as the main product according to the equations:



Although our short-term experiments failed to reveal tin oxide by X-ray diffraction, examination of an aged catalyst after long-term activity testing (see below)

Smaller amounts of coproducts, depending on the catalyst and conditions, were butanol, 2-ethyl-hexanal and a 12-carbon compound.

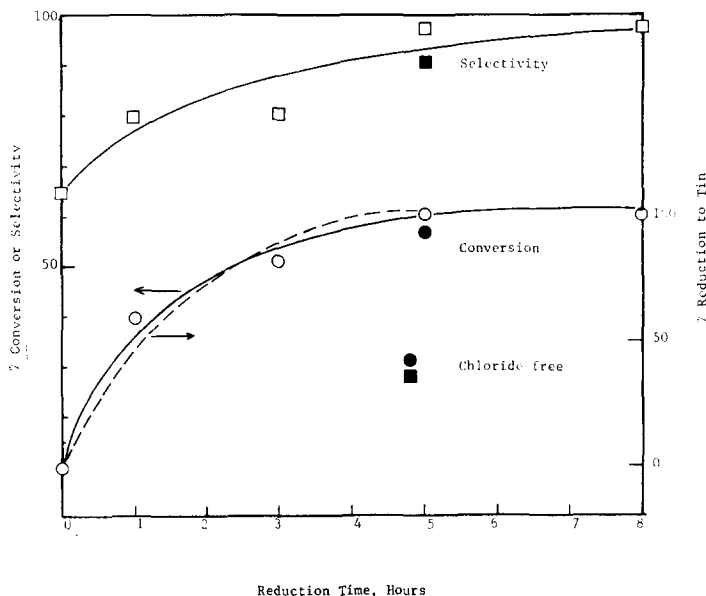
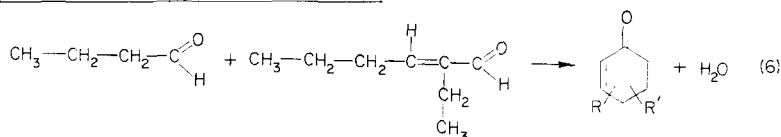


Fig. 5. Effect of catalyst reduction time at 375°C on catalyst activity: reaction temp. = 250°C; iso-butylaldehyde LHSV = 0.5; and hydrogen-to-isobutylaldehyde ratio = 2.

The catalyst must be activated by pretreatment with hydrogen. The effect of the hydrogen pretreatment is illustrated in Fig. 5, which shows the conversion and selectivity as a function of the time the catalyst has been pretreated with hydrogen at 375°C and atmospheric pressure. The non-reduced catalyst exhibited very low activity and poor selectivity. However, by increasing the prereluction time both the conversion and selectivity were increased. Conversion follows closely the degree of reduction of the catalyst under the same conditions as shown in Fig. 5; the latter curve was constructed from the catalyst reduction data. Further reduction beyond 8 hr had no beneficial effect. The pretreatment time could be reduced by increasing the temperature and/or increasing the hydrogen pressure. For example, the maximum activity

small amount of chloride, a chloride-free catalyst was also tested. This catalyst gave about the same activity as one prepared from stannous chloride, as shown in Fig. 5. Thus, chloride is not the active component in the catalyst.

The variation of the catalytic activity with tin content is shown in Fig. 6. Catalytic activity increased up to 10 wt % tin and further addition of tin did not result in an increase of activity. It was interesting to find that the concentration of the main undesirable product increased to a maximum value of 8 wt % of the organic condensate with a 40 wt % tin-silica catalyst. The undesirable product was identified to be a 12-carbon unsaturated cyclic ketone which is most likely formed by a reaction between *n*-butylaldehyde and 2-ethyl-hexenal [Eq. (6)].



was obtained by reducing the catalyst for only 4 hr at 500°C, although 1 hr would probably be sufficient according to the reduction data.

Since the standard catalyst contained a

This material was identified by a combination of mass and infrared spectroscopy. The identities of R<sub>1</sub> and R<sub>2</sub> and their positions on the ring have not been established.

Conversion and selectivity values as a

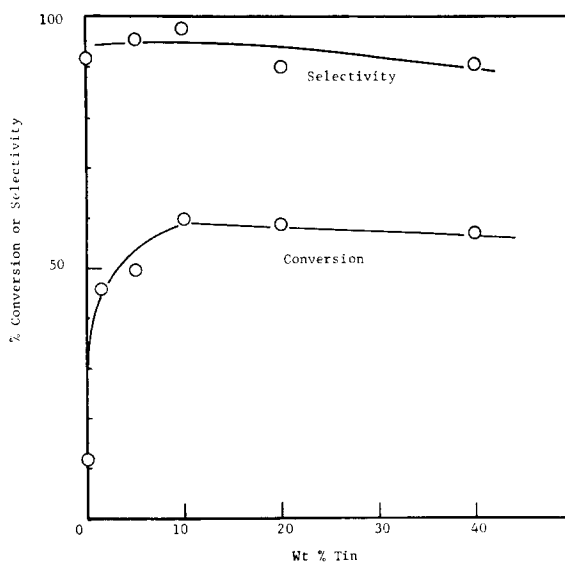


FIG. 6. Effect of tin concentration on conversion and selectivity: reaction temp. = 250°C; isobutyraldehyde LHSV = 0.5; hydrogen-to-isobutyraldehyde ratio = 2; and catalyst reduced 6 hr at 375°C.

function of contact time at 250°C are depicted in Fig. 7. Over the contact time studied the selectivity was always greater than 90%, and at the lowest contact time the selectivity reached a value of 98%. Calculations by us showed that the aldol condensation reaction is equilibrium limited at a conversion of approximately 75%, which

is in good agreement with that found experimentally.

In order to efficiently carry out the condensation reaction, i.e., at good conversions, selectivities, and catalyst life, a hydrogen atmosphere had to be used. Using a hydrogen:butyraldehyde ratio of two at 1 LHSV, 250°C, and at atmospheric pressure,

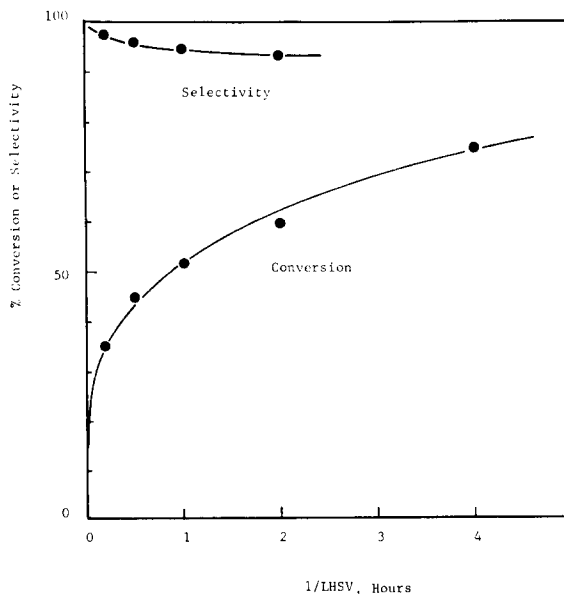


FIG. 7. Conversion and selectivity as a function of space time: reaction temp. = 250°C; hydrogen-to-isobutyraldehyde ratio = 2; catalyst = 10 wt % tin-on-silica; and catalyst reduced 6 hr at 375°C.



slow catalyst aging occurred. Examination of the deactivated catalyst by X-ray diffraction showed that a considerable amount of the tin was in the form of  $\text{SnO}_2$ . By increasing the hydrogen:butyraldehyde ratio to five, the tin was maintained in the reduced state with no catalyst aging over 15 days of continuous operation.

In order to obtain high selectivity, it is critical that silica gel be used as the support. Several other supports were tested and found very much inferior, as shown by the data in Table 2. These data were obtained

TABLE 2  
EFFECT OF SUPPORT<sup>a</sup>

Support	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>	Surface area (m <sup>2</sup> /g)
$\gamma$ - $\text{Al}_2\text{O}_3$	17	84	162
$\eta$ - $\text{Al}_2\text{O}_3$	22	42	256
Filtrol $\text{Al}_2\text{O}_3$ + 1% Na	7	72	147
5A Molecular Sieve	19	63	137
Magnesium-Aluminate	20	86	100
Filtrol $\text{Al}_2\text{O}_3$	22	77	205
Harshaw $\text{Al}_2\text{O}_3$	19	78	231

<sup>a</sup> All catalysts contained about 10 wt % tin, pretreated in  $\text{H}_2$  for 5 hr at 375°C.

<sup>b</sup> Temp., 250°C, LHSV = 1.

after the catalysts were pretreated with hydrogen for 5 hr at 375°C and the butyraldehyde was passed over at a LHSV of 1 at 250°C. Under these conditions, the tin-silica catalyst gave a 50% conversion with a 96% selectivity. Reasons for lower activities found on other supports may be lower tin surface areas, tin-support interactions, or incomplete reduction of the tin oxide.

#### DISCUSSION

The major discovery reported in this paper is that a tin-silica catalyst can be activated to give high yields of 2-ethylhexenal for the aldol condensation of *n*-butyraldehyde. There have been several reports on the activation of silica for aldol condensation reactions by the addition of other metal oxides. In a recent paper by Young and Sheppard (10) on infrared studies of acetaldehyde adsorbed on silica, crotonaldehyde was observed on the sur-

face and its formation was attributed to the acidity of the surface hydroxyl groups. The mechanism proposed for this condensation involved a surface catalyzed keto-enol tautomerism, followed by an addition reaction between the enol form and a protonated molecule to give acetaldehyde. The acetaldehyde then dehydrated to crotonaldehyde and water. In this same paper references were cited on the use of other treated silica catalysts and Young and Sheppard attributed the activation of silica by adding these metal oxides to an increase in surface acidity, thus making these combined oxides more effective than silica.

The ammonia adsorption measurements showed the activated tin catalysts to have a threefold higher surface acidity at 250°C (reaction temperature) than the silica base, and there is also approximately a fivefold increase in catalytic activity of the reduced tin-silica catalyst compared to the silica base. Based on these results the increase in activity could be partly explained by the increase in surface acidity. However, the fact that the silica base and the calcined catalyst exhibit the same activity (see Figs. 1 and 4) but yet have different surface acidities sheds doubt that surface acidity (as determined by ammonia adsorption) is mainly responsible for the high activity of the reduced tin catalyst.

The possibility of a direct reaction of butyraldehyde with either tin or stannous oxide to form a surface complex which reacts with a second molecule of butyraldehyde to form 2-ethylhexenal has to be considered. Recently, Hemidy and Gault (11) reported that butyraldehyde cracks to propane and propylene over metallic palladium and Tsuji *et al.* (12) suggested that the butyraldehyde reacts directly with metallic palladium to form surface acyl and alkyl complexes. Bulk tin and stannous oxide were tested for the condensation reaction by us and both were found essentially inactive, giving less than 2% conversion. However, the low activity does not rule out the possibility that either tin or stannous oxide dispersed on silica can be the active species because the surface areas of the bulk materials were quite low, less than

1 m<sup>2</sup>/g. Unsuccessful attempts were made to prepare a high surface area sample of stannous oxide to test for catalytic activity.

An explanation for the formation of stannic oxide over a period of time might be due to oxidation of the tin with water. Water is a major product of the condensation reaction and would be present in appreciable concentration during steady-state operation. Under these conditions, thermodynamics are favorable for oxidation of the tin, and although the oxidation rate is low, over a period of time, gradual oxidation could occur. Higher concentrations of hydrogen would suppress this reaction.

Sabatier (13) reported that stannous oxide acts as an alcohol dehydrogenation catalyst at about 300°C but is slowly reduced to metallic tin, and as the reaction proceeds the globules of metal coalesce into larger globules with a loss of activity. The reaction described in this paper is actually carried out above the melting point of tin. One would suppose that during reaction the liquid tin dispersed on the silica support would coalesce into larger droplets of tin metal with a gradual loss of catalytic activity. The  $\beta$ -tin crystallites observed at room temperature on the reduced tin-silica catalysts by X-ray diffraction were fairly large, approximately 500 Å.

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