

## Selective Disproportionation of Olefins Using Thallium Treated Molybdenum-Alumina Catalysts

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Addition of thallium to alumina results in a reduction of surface acidity (as measured by ammonia adsorption) and the inhibition of double-bond isomerization. Adding thallium to molybdenum-alumina results in the promotion of high selectivity for olefin disproportionation. There are numerous reports of the addition of Group Ia and IIa metals to molybdenum-alumina to promote this selectivity. It has been found that thallium is equivalent to rubidium on a molar basis in its effectiveness for promoting olefin disproportionation selectivity. There is a linear relationship between this selectivity and the ionic radius of monovalent thallium and Group Ia ions. It is suggested that the polarizability of the cation is important for reducing surface acidity. At reaction temperature, there is a linear correlation between ammonia adsorption and disproportionation selectivity.

### INTRODUCTION

Since Banks and Bailey (1) reported the first olefin disproportionation reaction in 1964, numerous other reports on this reaction have appeared. A 1969 review article by Bailey (2) discusses the significant factors, such as catalysts and processing conditions, for various olefin disproportionation reactions. The reaction mechanism has been the subject of several papers (3-5).

In most cases molybdenum, tungsten or rhenium oxides is the salient catalyst component. Propylene has been studied most extensively, yielding predominantly ethylene and butenes. Higher  $\alpha$ -olefins yield a complex product mixture due to auxiliary isomerization of starting material and products. The selectivity to ethylene and one higher olefin can be increased by reducing isomerization activity of the catalyst. In all cases reported the selectivity has been increased by adding a small amount of alkali or alkaline earth metal oxide to the catalyst. Potassium and sodium oxides appear to be the compounds most commonly used (2, 6).

During our investigation of catalysts for the disproportionation of  $C_4$  and higher

olefins, it was found that the addition of thallium to a molybdenum-alumina catalyst resulted in a considerable increase in reaction selectivity.

This paper reports the data concerning thallium treated molybdenum-alumina catalysts for the disproportionation of 1-butene and 1-octene. The effectiveness of thallium for improving selectivity is compared to Group Ia metal oxides, and oxides of the same group as thallium.

### EXPERIMENTAL METHODS

#### *Catalysts*

The catalysts used in this study were prepared by impregnating Ketjen  $\gamma$ -alumina (300  $m^2/g$ ) with an aqueous solution of ammonium paramolybdate to the point of incipient wetness. The base catalyst consisted of 13 wt %  $MoO_3$  (8.6 wt % Mo). After impregnation the catalyst was dried at 120°C for 16 hr and then calcined for 16 hr at 550°C. The surface area of this catalyst was 252  $m^2/g$ . Catalysts treated with thallium and the Group Ia ions were prepared by impregnating the calcined molybdenum-alumina catalyst. The salts used in dilute

aqueous solution were thallium nitrate, thallium acetate, lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium nitrate and cesium nitrate. Sodium and potassium hydroxides were obtained from Fisher, the others from Alfa Inorganics, Inc. After addition and calcination of catalysts containing 2 wt % Tl, Na, K, Rb and Cs, the surface areas were 226, 231, 229, 225 and 227 m<sup>2</sup>/g, respectively. The concentration of thallium and other Group Ia metals on the finished calcined catalysts were determined by atomic absorption spectrophotometry using the Jarell Ash 82-5000 spectrophotometer. Catalyst surface acidity was determined by ammonia gas adsorption on 1 g catalyst samples at 175°C. After sample evacuation, the amount of ammonia desorbed over the temperature range 175 to 500°C was measured. The method is described in detail by Barth and Ballou (7).

#### Reaction Procedures

The reactants used were butene-1 and octene-1. Butene-1 (99% purity) was obtained from the Phillips Petroleum Company. High purity octene-1 was prepared in our laboratory and was stored prior to use over 4-A molecular sieves under a nitrogen atmosphere.

For the butene-1 experiments, a  $\frac{3}{8} \times 12$  in. stainless steel reactor was used. Ten milliliters of 20 to 40 mesh catalysts were loaded into the middle section of the reactor with the space above and below the catalyst filled with quartz chips. The flow of the feed was downflow. For octene-1, a  $1 \times 12$  in. quartz reactor was used. Twenty milliliters of 20 to 40 mesh catalysts were loaded in the upper part of the reactor with the lower portion filled with quartz chips. The octene-1 was passed upflow into the reactor.

A constant temperature with a maximum variation of  $\pm 1.5^\circ\text{C}$  was maintained by an automatic temperature controller. Heating was done with a concentric electric furnace. The temperature of the catalyst bed and preheat zone was monitored by a multi-point recorder connected to an iron-constantan thermocouple in the reactor. Butene-1 was fed from a pressure cylinder

through a pressure regulator, Brooks rotometer and needle valve. Octene-1 was delivered by a Milton Roy Company mini-pump. Reactants, nitrogen and air used for activation of the catalyst were passed individually through  $1 \times 10$  in. columns filled with activated A-4 molecular sieves, and the moisture content was monitored with a DuPont moisture analyzer. Whenever the moisture content of the streams exceeded 10 ppm, the molecular sieves were reactivated. The catalysts were activated *in situ* prior to the reaction. The activation procedure consisted of catalyst calcination for 16 hr at 500°C in a stream of air after which the reactor was purged with nitrogen at 500°C for 1 hr. Nitrogen flow was maintained while the reactor was cooled to reaction temperature. The flow rate of air and nitrogen during the activation period was maintained at 100 ml/min. Following catalyst activation, the olefin flow was initiated, and the whole system was equilibrated for 1 hr before taking samples for analysis. The butene-1 experiments were carried out at a butene-1 gas hourly space velocity of 1000, 140°C and a butene-1 partial pressure of 1 atm. The octene-1 experiments were carried out at a liquid hourly space velocity of 2.5, 120°C and without an added diluent.

All reaction products were analyzed using a F & M model gas chromatograph with a  $\frac{3}{16}$  in. o.d. column, 20 ft long, packed with 5% OV-1 silicon oil on Gas-Chrom Q supplied by Applied Science Laboratories. All products of the butene-1 reaction were injected without separation by a Carle microvalve heated to 200°C. Separation of butene isomers was facilitated by the use of a liquid nitrogen loop in the column (8). Gaseous and liquid products of octene-1 reaction were collected and analyzed separately. In the latter case, the total volume of the gaseous products was recorded.

## RESULTS

### Reaction Studies

Table 1 presents data demonstrating the low selectivity to the expected products that is obtained using a 13% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>

TABLE 1  
DISPROPORTIONATION OF BUTENE-1 AND OCTENE-1 WITH THALLIUM AND POTASSIUM-TREATED  
MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> CATALYSTS<sup>a</sup>

| Feed<br>Added metal (2 wt %):             | Butene-1 |      |      | Octene-1 |      |      |
|---|----------|------|------|----------|------|------|
|   | —        | Tl   | K    | —        | Tl   | K    |
| Conversion (mole %)                       | 19.4     | 9.1  | 9.3  | 95.3     | 46.1 | 49.3 |
| Product distribution (mole %)             |          |      |      |          |      |      |
| Ethylene                                  | 7.5      | 39.6 | 44.1 | 7.2      | 41.2 | 43.6 |
| Propylene                                 | 39.6     | 8.8  | 4.5  | 7.8      | 1.0  | 1.1  |
| Butenes                                   | —        | —    | —    | 6.2      | 0.1  | 0.1  |
| Pentenes                                  | 29.7     | 8.2  | 4.7  | 6.3      | 0.1  | —    |
| Hexenes                                   | 14.5     | 41.4 | 46.2 | 6.4      | 0.3  | 0.3  |
| Heptenes                                  | 5.1      | 1.3  | 0.5  | 8.0      | 0.9  | 0.8  |
| Octenes                                   | 3.1      | 0.7  | —    | —        | —    | —    |
| Nonenes                                   | 0.5      | —    | —    | 10.2     | 2.5  | 1.5  |
| Decenes                                   | —        | —    | —    | 5.3      | 0.3  | 0.2  |
| C <sub>11</sub>                           | —        | —    | —    | 4.4      | 0.1  | 0.1  |
| C <sub>12</sub>                           | —        | —    | —    | 7.2      | 0.7  | 0.2  |
| C <sub>13</sub>                           | —        | —    | —    | 11.5     | 4.7  | 3.2  |
| C <sub>14</sub>                           | —        | —    | —    | 10.7     | 47.8 | 48.0 |
| C <sub>15</sub>                           | —        | —    | —    | 7.1      | 1.2  | 0.7  |
| Higher                                    | —        | —    | —    | 1.7      | 0.4  | 0.2  |
| C <sub>2</sub> + C <sub>6</sub> (mole %)  | 22.0     | 81.0 | 90.3 | —        | —    | —    |
| C <sub>2</sub> + C <sub>14</sub> (mole %) | —        | —    | —    | 17.9     | 89.0 | 91.6 |

<sup>a</sup> Base MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst contains  $9 \times 10^{-4}$  moles of Mo/g of catalyst.

catalyst for the disproportionation of butene-1 and octene-1. These data also show that the higher the carbon number of the starting olefin, the lower the selectivity to a single higher molecular weight olefin. The main products of butene-1 disproportionation are propylene (39.6%) and pentenes (29.7%). For octene-1 disproportionation only 10.7 mole % of tetradecene-7 was formed. Significant amounts of nonenes and tridecenes were in the product indicating that octene-1 reacts mainly with octene-2 in head-to-head and head-to-tail configurations.

The addition of thallium to MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> resulted in a significant increase in selectivity to ethylene and a single higher disproportionated product. The effect of thallium on disproportionation selectivity is compared in Table 1 with that of a potassium catalyst. The product distributions obtained with these catalysts are very similar. These data show that the addition of 2% thallium increased the ethylene + hexene-3 molar yield from 22.0 to 81.0% for butene-1

and the ethylene + 7-tetradecene yield from 17.9 to 89.0% for octene-1. Additional thallium did not effect a substantial improvement in selectivity as shown by the data for the disproportionation of butene-1 and octene-1 in Fig. 1. The greatest percentage gain in selectivity was obtained by adding between 0.5 to 2% thallium to MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. The conversion declined linearly with thallium content over the range studied. This figure also shows the percentage of butene-2 in the recovered butene fraction from the disproportionation of butene-1 as a function of thallium content. Since the selectivity increased with thallium content, the amount of butene-2 formed decreased as expected.

The addition of 2% gallium or indium, both of the same periodic group as thallium, resulted in no selectivity improvement when added to MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. This is shown in Fig. 2 where several catalysts are compared for the octene-1 reaction. Similar results were obtained for butene-1 disproportionation. The selectivity declines with

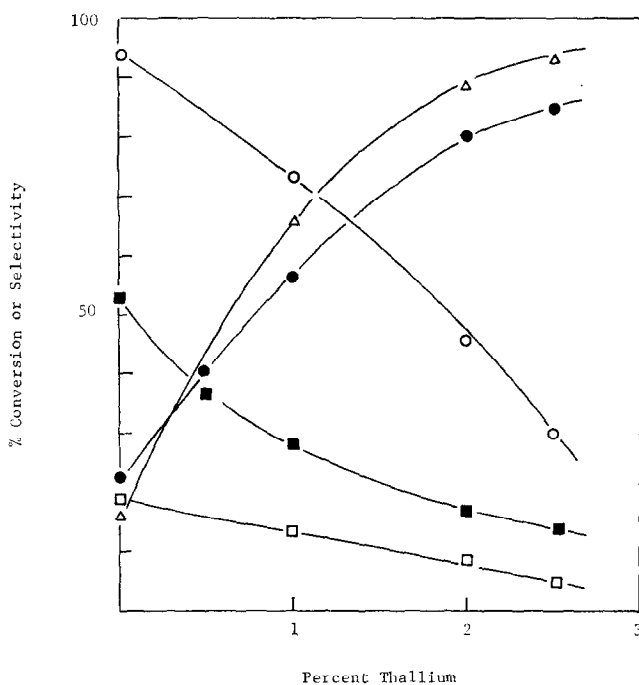


FIG. 1. Butene-1-octene-1 conversion and selectivity values as a function of thallium content: (□) butene-1 conversion, (●) selectivity to C<sub>2</sub> + C<sub>6</sub>, (■) butene-2 in product, (○) octene-1 conversion and (△) selectivity to C<sub>2</sub> + C<sub>14</sub>.

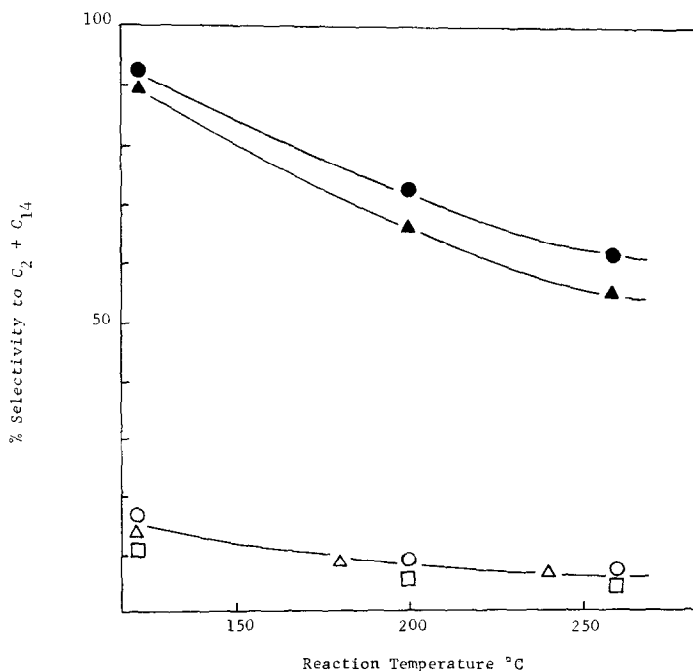


FIG. 2. Octene-1 disproportionation selectivity to C<sub>2</sub> + C<sub>14</sub> as a function of temperature and catalyst: (○) MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>; (△) Ga-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>; (□) In-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>; (●) K-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>; (▲) Tl-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>.

increasing temperature are probably due to a higher activation energy for isomerization than for disproportionation. This is verified by the increase in the percentage of butene-2 in the recovered butenes from the disproportionation of butene-1 with increasing reaction temperature.

Several other metal ions were evaluated while attempting to improve disproportionation selectivity of  $\text{MoO}_3/\text{Al}_2\text{O}_3$ . Mercury, lead, tellurium and various rare earths to name a few gave no significant selectivity improvement. Thus, only a select number of ions in combination with  $\text{MoO}_3/\text{Al}_2\text{O}_3$  gives high selectivity.

It is well documented in the literature (2) that the addition of Groups Ia and IIa metal oxides to  $\text{MoO}_3/\text{Al}_2\text{O}_3$  and tungsten-alumina oxide catalysts enhances disproportionation selectivity. In most cases potassium and sodium oxides have been used. Results we obtained with 2 wt % potassium-13%  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst verified the improvement in selectivity that can be obtained. The data given in Table 1 shows that at the 2% level, potassium is more ef-

fective than thallium for improving selectivity. The difference between potassium and thallium at this concentration is greater for the disproportionation of butene-1 than for octene-1.

In order to obtain a more quantitative comparison of the effectiveness of thallium with other Group Ia metals, a series of experiments were performed in which octene-1 and butene-1 disproportionation reactions were carried out using Li, Na, K, Rb, Cs and Tl- $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts. Figure 3 shows the data obtained for the disproportionation of butene-1 as a function of the molar concentration of these ions on  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts. Because of the curve shapes, good comparisons of the abilities of the metals to improve selectivity could only be made within the 60 to 80% range. Within this range the order of effectiveness was  $\text{Cs} > \text{Tl} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ . Figure 4 shows the percentage of butene-2 in the recovered effluent butenes from the same experiments. At all metal levels, the ability to suppress butene-2 formation is in the order:  $\text{Cs} > \text{Rb} > \text{Tl} > \text{K} > \text{Na} > \text{Li}$ .

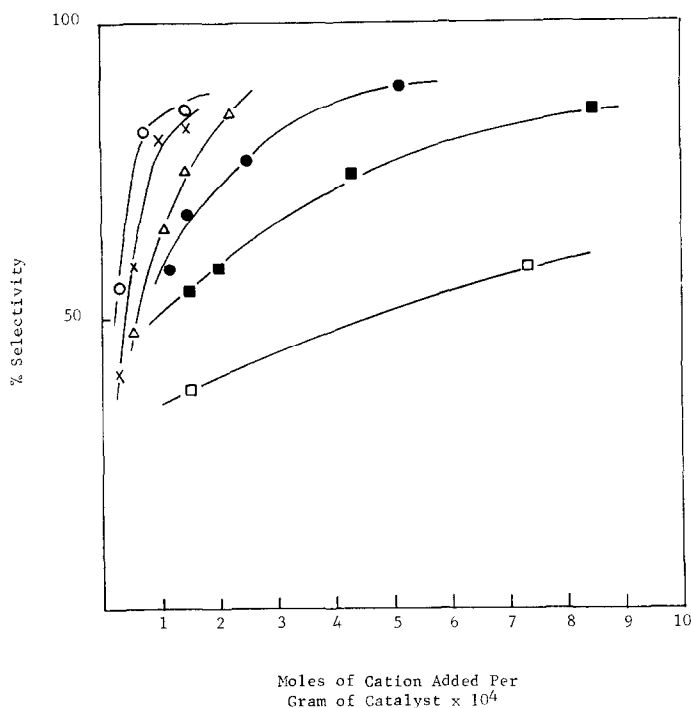


FIG. 3. Selectivity of 1-octene disproportionation as a function of Li, Na, K, Rb, Cs and Tl concentrations: ( $\square$ ) Li, ( $\blacksquare$ ) Na, ( $\bullet$ ) K, ( $\triangle$ ) Rb, ( $\times$ ) Tl, ( $\circ$ ) Cs.

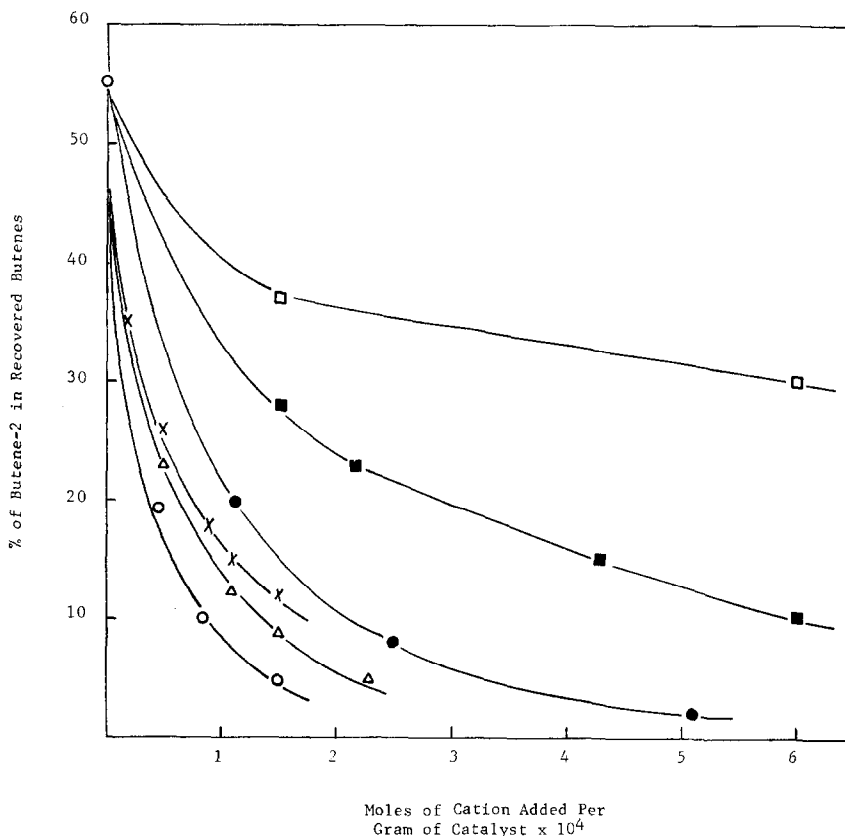


FIG. 4. Mole % of butene-2 in recovered butenes from the disproportionation of butene-1 as a function of Li, Na, K, Rb, Cs and Tl concentrations: ( $\square$ ) Li, ( $\blacksquare$ ) Na, ( $\bullet$ ) K, ( $\times$ ) Tl, ( $\triangle$ ) Rb, ( $\circ$ ) Cs.

### Catalyst Studies

Catalysts were prepared using both thallium (I) nitrate and thallium (I) acetate as starting salts. There was no noticeable difference in conversion and selectivity from catalysts made from these salts. Various catalysts were analyzed to determine if the amount of thallium retained on the catalysts after calcining at  $500^\circ\text{C}$  was the same as that impregnated. Catalysts intended to have 1 and 2% thallium were found to contain 0.92 and 1.90%, respectively. Thus, very little or no thallium is lost upon calcination at  $500^\circ\text{C}$  in air. This was a point of concern especially for samples prepared from  $\text{TlNO}_3$ , for it is reported that  $\text{TlNO}_3$  boils at  $430^\circ\text{C}$  (9).

A catalyst prepared by impregnating  $\text{Al}_2\text{O}_3$  with an aqueous solution of  $\text{TlNO}_3$  to give 8% thallium after calcination at  $500^\circ\text{C}$  was examined by X-ray diffraction. The dif-

fraction pattern of this sample resembled that of a poorly crystallized  $\gamma$ -alumina. There was no indication of any crystalline thallium compound. Some of the lines which normally appear in the pattern for  $\gamma\text{-Al}_2\text{O}_3$  were not clearly resolved from the background. Its general characteristics suggest that the  $\text{Al}_2\text{O}_3$  lattice was even more disordered than  $\gamma\text{-Al}_2\text{O}_3$  normally is. This same phenomenon was observed when the alumina was impregnated with  $\text{KNO}_3$  or  $\text{NaNO}_3$  and then calcined at  $500^\circ\text{C}$ . The 8% thallium-alumina catalyst was white after calcination at  $500^\circ\text{C}$  for 24 hr. Calcining  $\text{Tl}(\text{NO}_3)_3$  and  $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)_3$  at  $500^\circ\text{C}$  for 24 hr gave a brown-black material which exhibited X-ray lines attributed to crystalline  $\text{Tl}_2\text{O}_3$ . It was surprising to find that this calcination gave only  $\text{Tl}_2\text{O}_3$  since it has been reported that  $\text{Tl}_2\text{O}_3$  begins to lose oxygen at about  $100^\circ\text{C}$  to give  $\text{Tl}_2\text{O}$  (10). The

fact that the thallium-alumina catalyst is white after calcination suggests that thallium behaves differently when dispersed on alumina compared to bulk thallium oxides.

NH<sub>3</sub> adsorption measurements were carried out on 13% Mo/Al<sub>2</sub>O<sub>3</sub> and catalysts made by adding enough thallium to this base to give catalysts containing 0.5, 1.0, 1.5, 2.0 and 2.5 wt % thallium. All of these samples were treated in the same manner, i.e., high temperature dry air calcination at 500°C. The NH<sub>3</sub> adsorption was measured between 170–500°C. At 170°C the amounts adsorbed were quite different. However, as the adsorption temperature was increased the quantities of NH<sub>3</sub> adsorbed converged. Figure 5 gives the amount of NH<sub>3</sub> adsorbed at 170°C as a function of butene-1 and octene-1 disproportionation selectivities for the catalysts containing various amounts of thallium. This plot shows that selectivity for butene-1 disproportionation at 140°C varies inversely with the amount of NH<sub>3</sub> adsorbed. For octene-1 disproportionation

at 120°C, there is some scatter but basically the same linear relationship was found as for butene-1. Extrapolation of the NH<sub>3</sub> adsorption curves to the reaction temperatures gave the same relationships. Thus, NH<sub>3</sub> adsorption at or near reaction temperature of the thallium-treated catalysts defines what disproportionation selectivity can be expected.

### DISCUSSION

The thallos ion is a very effective depressant of surface acidity (as measured by NH<sub>3</sub> adsorption), an inhibitor of double-bond isomerization and a promoter of disproportionation selectivity. The effectiveness of thallium as an inhibitor (or promoter) was then compared to Li, Na, K, Rb, and Cs. To achieve the same double-bond isomerization inhibition or disproportionation promotion different molar amounts of each particular metal had to be used as shown in Figs. 3 and 4. The effectiveness of the Group Ia ions as isomeri-

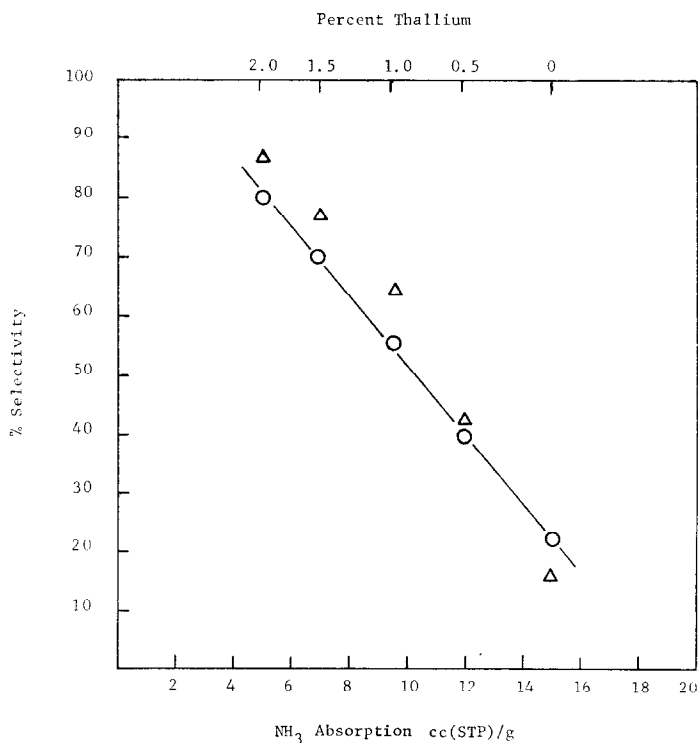


Fig. 5. Percentage selectivity for butene-1 and octene-1 disproportionation as a function of ammonia adsorption at 170°C on catalysts containing different levels of thallium: (○) butene-1; (△) octene-1.

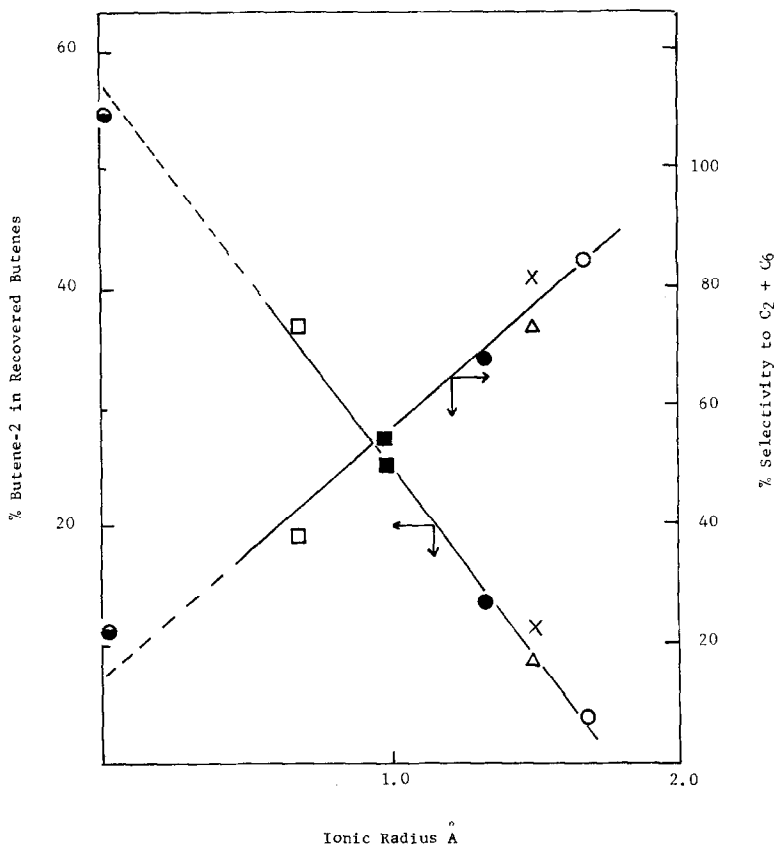


Fig. 6. Mole % butene-2 in recovered butenes and mole % selectivity of butene-1 disproportionation to  $C_2 + C_6$  as a function of the ionic radius of the various metals added to  $MoO_3/Al_2O_3$ : ( $\ominus$ )  $MoO_3/Al_2O_3$ ; ( $\square$ )  $Li-MoO_3/Al_2O_3$ ; ( $\blacksquare$ )  $Na-MoO_3/Al_2O_3$ ; ( $\bullet$ )  $K-MoO_3/Al_2O_3$ ; ( $\triangle$ )  $Rb-MoO_3/Al_2O_3$ ; ( $\times$ )  $Tl-MoO_3/Al_2O_3$ ; ( $\circ$ )  $Cs-MoO_3/Al_2O_3$ .

zation inhibitors or promoters for disproportionation selectivity increased linearly according with ionic radius. This relationship is shown in Fig. 6 which shows that both the percentage of butene-2 in the recovered butenes and the disproportionation selectivity to ethylene and hexene-3 are linear functions of the ionic radius of the added cation at a level of  $1.5 \times 10^{-4}$  moles/g of catalyst. All of these catalysts contained the same amount of molybdenum, i.e., approximately  $9 \times 10^{-4}$  moles/g of catalyst. From the data in Figs. 3 and 4, it is obvious that deviations above or below the  $1.5 \times 10^{-4}$  moles/g level can give a nonlinear relationship. The data in Fig. 6 show that the effectiveness of thallium as an isomerization inhibitor or a promoter for disproportionation selectivity is com-

parable with rubidium and both of these ions have essentially the same ionic radius of 1.47 Å in the monovalent state. Thallium can also exist in the +3 valence state, with an ionic radius of 0.95 Å. The linear relationships shown in Fig. 6 strongly suggests that thallium is present in the thallos state. The chemistry of thallium is dominated by the monovalent state because of the inert pair in its valence shell ( $6S^26P$ ). With gallium and indium the +3 oxidation state is preferred (10) which is the probable reason why they have no effect on disproportionation selectivity or double-bond isomerization when added to molybdenum-alumina.

Alumina, predried above 400°C, readily catalyzes double-bond isomerization at room temperature (11). This is the most



probable cause of the low disproportionation selectivity when a molybdenum-alumina catalyst is used. The nature of the alumina site and mechanism responsible for the double-bond isomerization of olefins has been a point of controversy for some time (12-15).

There are many reports throughout the literature that the surface acidity of solid acid catalysts can be decreased by the addition of small quantities of alkali and/or alkaline earth metals. Most of the reports apply to catalytic cracking using silica-alumina catalysts and early workers suggested that a metathesis takes place between the alkali metal ions of an aqueous solution and the protons of the catalyst surface. However, Hirschler (16) reported that the effect of aqueous KOH on the acidity of silica-alumina does not result in a simple replacement of protons with complete neutralization and disappearance of acid sites. Rather, there is a modification of surface acid sites distribution. Parera and co-workers (17) recently reported that addition of a small amount of NaOH to silica-alumina results in a sharp fall in strong acidity. At the same time, the weak acidity increases keeping the total acidity constant. The amount of NaOH necessary to eliminate the acidity stronger than 90%  $H_2SO_4$  is greater than the value of this acidity as measured with *n*-butylamine at room temperature. It was suggested that this might indicate that NaOH does not absorb in a very selective manner; part of it goes to sites which are not acidic.

Hall, Lutinski and Gerberich (18) reported that base exchange of silica-alumina with alkali metal ions reduces catalytic activity but does not markedly affect the hydrogen content. With alumina, the rate of isomerization correlated inversely with hydroxyl content and with deuterated alumina, the appearance of deuterium in the 2-butenes was small and decreased with increasing dehydration temperature. Based on these observations, Hall, Lutinski and Gerberich (18) suggested that the effect of base exchange is not a metathesis with catalyst protons but an incorporation of a basic oxide into the catalyst structure resulting

in a decrease in Lewis acidity, i.e., a reduction in the strength as well as the number of Lewis sites.

We suggest that adding thallium or any Group Ia metal reduces surface acidity and thus olefin isomerization in two major ways. First, the added salt combines with a Lewis or dual acid-base site. The cation would combine with the oxide ion and the anion with the exposed aluminum ion and be incorporated into the structure as suggested by Hall, Lutinski and Gerberich (18). In the case of decomposable salts such as KOH or  $KNO_3$ , the final form would be  $K_2O$ . Salt addition to alumina would be random where an equivalent amount of salt would not neutralize an equivalent number of acid-base sites. The remainder of the salt would deposit on other areas of the alumina surface.

Addition of  $1.5 \times 10^{-4}$  moles of thallium/g of alumina would result in  $3 \times 10^{13}$  thallium ions/cm<sup>2</sup> of surface. Assuming cubic close packing of the alumina surface, there would be approximately  $1.5 \times 10^{15}$  hydroxyl sites/cm<sup>2</sup>. This would give 3 thallium ions/150 hydroxyl sites or roughly 2% coverage of the surface. Based on work reported by Peri (15), dehydration at 500°C of the alumina would result in 20% of the sites as hydroxyl, 40% as exposed aluminum ion and the rest as oxide ions. There would then be potentially  $6 \times 10^{14}$  ion pair sites available. Thus, with  $1.5 \times 10^{-4}$  moles of thallium, one out of every 20 sites would be covered or only 5% of the surface sites destroyed. Yet it is clear that this is sufficient to materially suppress double-bond isomerization.

Besides direct neutralization by combination or blockage there is another effect dependent on the size of the added ion. As shown herein, the decrease in olefin isomerization and increase in disproportionation selectivity increased with the size of the added ion. It is suspected that reduced surface acidity with increasing cation size corresponds to the increased polarizability associated with the increased cation size. As the alumina surface is covered with large polarizable cations, areas of high surface charge density associated with the acid

sites of the alumina will be reduced in intensity. In effect, the result would be similar to that reported by Hirschler (16) and Parera *et al.* (17), i.e., that the addition of KOH and NaOH eliminates strong acidity while increasing the amount of weaker acid sites.

Danforth (19) and Danforth and Martin (20) found that large alkali metal ions are more effective poisons per ion than the small alkali metal ions for catalytic cracking and that the poisoning effect is a function of the radius of the ions. In this work it was suggested that adjacent sites must be so close that a single large alkali ion can cover or make inaccessible more than one active site. Hirschler (16) also found that the reduction in strong acidity increased with the size of the ion within a given group of the periodic table. Since the size difference in going from Li to Cs is approximately 1 Å, it is unlikely that decreased surface acidity is due to the physical blockage of adjacent sites as suggested. Rather, the charge polarization mechanism is probably responsible for the decrease in activity with ionic size.

The addition of thallium to molybdenum alumina gives a decrease in surface acidity as shown by the ammonia adsorption data in Fig. 5. The effectiveness of thallium in reducing surface acidity is comparable with that of the higher Group Ia metals on a molar basis. These data were obtained at 170°C where the differences in adsorptivity by the catalysts were large. At higher temperatures, the ammonia adsorption curves converge with the differences between the adsorption capabilities of the catalysts diminishing. When using ammonia adsorption, it is best to use low temperatures since at temperatures greater than 200°C ammonia effects the loss of water of constitution at 250–300°C which alters the number and types of acid sites (21).

From the data in Fig. 5, it was calculated that it takes approximately 25 thallium ions to decrease ammonia adsorption at 170°C by 1 ammonia molecule/g of catalyst. This was determined by calculating the decrease in the molecules of ammonia adsorbed by increasing the thallium content from 0.5 to

1.0, 1.0 to 1.5 and 1.5 to 2.0 wt %. This supports our original suggestion, and that of others, that the addition of thallium or any other Group Ia or IIa metal to alumina results in a random surface coverage with little or no tendency of the added ion to be attracted to a particular type of site or surface.

The relationship shown in Fig. 5 is not too surprising if one assumes that ammonia adsorbs on the alumina at the exposed alumina ion of an acid–base type site (15), and that this site is responsible for isomerization. Thus, as thallium is added these sites are blocked giving reduced ammonia absorption and olefin isomerization with a corresponding increase in disproportionation selectivity. The linear relationship in Fig. 5 may be fortuitous. However, to our knowledge this is the first reported case of a correlation between ammonia adsorption and a reaction parameter. Wilmot, Barth and MacIver (22) found that acidity as measured by ammonia adsorption did not correlate with selectivity or activity of solid acid catalysts for olefin isomerization, and Peri (15) concluded that attempts to relate total ammonia retention on alumina to catalytic activity appears destined to very limited success.

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