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Effect of Thallium on the Activity and Selectivity of Multicomponent Molybdate Catalyst for Selective Oxidation of 1-Butene

A number of catalysts for oxidative dehydrogenation have been proposed, and among the most effective is bismuth molybdenum oxide. Methods of increasing the activity and selectivity of this catalyst are of great practical and theoretical importance. One of the ways of increasing the effectiveness of bismuth molybdate is to prepare mixed catalysts with some transition metal oxides promoted mainly with phosphorus and alkali metals (*1*). As shown by the patent literature (*2–5*), thallium has proved to be a very efficient promoter for catalysts for partial oxidation of olefins, since when added in small amounts it changes considerably the properties of these catalysts. Because of this, a more detailed study is of interest. Recently Kobylinski and Swift (*6*) have shown that thallium added in small amounts to MoO_3/Al_2O_3 catalyst changes its selectivity in olefin disproportionation to a considerable extent.

The present experiments on the oxidation of butene-1 have been carried out in a flow system at temperatures in the range of 260–400°C. One milliliter (0.78 g) of catalyst crushed to size 16–28 mesh was placed in the reactor and a constant temperature (±1°C) was maintained by an automatic regulator. The gas composition was intermittently analyzed by two gas chromatographs connected sequentially and on-line with the reactor.

The catalyst, which was designed by the Catalytic Division of the Scientific Research Center of the Sumitomo Chemical Ltd. in Niihama City, Japan, was prepared by mixing solutions of the nitrate salts of the constituent metals (see below) with solutions of ammonium molybdate, phosphoric acid and silica sol. The mixture was evaporated to dryness and the residue was calcined at 300°C for 3 hr, cooled and crushed. The resulting powder was tabletted and calcined at 525°C for 6 hr to give an active catalyst composition. In the catalyst used in the present studies the components corresponded to the formula $Mo_{12}Ni_{4.5}Co_4Fe_1Bi_1P_{0.08}Tl_xO_{48.6}Si_{15}$, where $x = 0$–0.8. During a 90 day period the catalyst had constant activity and selectivity.

The catalyst composition used in this work is quite characteristic in containing thallium, and the catalytic activity and selectivity depend largely on the content of thallium. Compared with the corresponding catalyst containing no thallium, the present catalyst system accelerated the reaction rate of dehydrogenation and suppressed markedly the by-production of isomers, CO, CO_2 and oxygen-containing compounds. Figure 1 presents the relation between the amount of thallium contained in the catalyst (atomic%) and its activity as expressed by the degree of conversion of butene-1 to butadiene (curve 1), along with the selectivity (curve 2) and total conversion to CO_2 and CO at 310°C. The space velocity of the mixture was 810 hr^{-1} and the feed mixture composition was butene-1:air:steam in a molar ratio 1:19:19. These conditions correspond to those used in industrial reactors. Curves of activity and selectivity pass through a

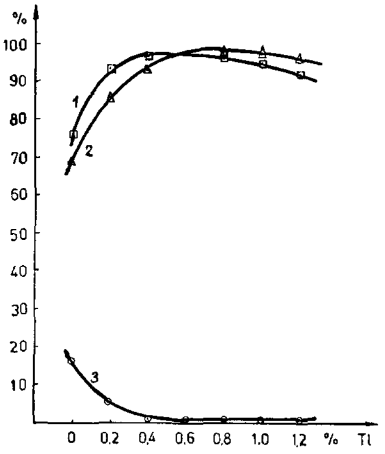

FIG. 1. Selectivity and activity to butadiene and to full oxidation as a function of the content of thallium in the catalyst.

maximum when the amount of thallium is 0.6%, while the total conversion to CO and CO_2 decreases with increasing thallium content and remains constant at approximately 1% when the amount of thallium is above 0.4%. In all cases the amounts of by-products such as alcohols, aldehydes and acids do not exeed 0.1%. The special feature of this catalyst is the low working temperature compared to other similar catalysts. Even at 260°C the catalyst with 0.6% Tl and the conditions stated gives 60% conversion and 94% selectivity. Figures 2 and 3 show the variations in activity and selectivity of the catalyst containing 0.6% thallium and the catalyst without thallium as a function of temperature, when a space velocity of 16,000 hr^{-1} and a feed composition of butene-1 : air : steam in a molar ratio of 1:13:16 were used.

The results show that the selectivity of the catalyst containing thallium remains practically constant in the range of 280–400°C with a small maximum at 310°C, whereas in the case of the catalyst containing no thallium the selectivity is lower and passes through a minimum at 310°C. With increasing space velocity of the feed mixture from 880 to 25,000 hr^{-1} the selectivity of the catalyst is not changed.

Surface acidity plays an important role in determining catalytic activity and selectivity. The change of acidity caused by addition of ammonia as an alkaline agent to the mixture can help the elucidation of this question. Figures 2 and 3 present curves of activity and selectivity of the catalysts with and without ammonia in the reaction mixture. In the case of the catalyst with 0.6% thallium, the addition of ammonia to the initial mixture reduces selectivity to a slight extent at low temperatures and does not change it at higher temperatures, whereas the catalytic activity in the presence of ammonia is lowered to a considerable extent. In the case of a catalyst containing no thallium, the addition of ammonia to the mixture results in a significant increase of selectivity, while a fall in the total activity, especially in the activity for isomerization, is also observed. Figure 4 shows the change in selectivity of the catalyst when the content of thallium is varied with presence of ammonia in the reaction mixture (curve 1) and with no ammonia (curve 2). If the catalyst contains a low amount of thallium the addition of ammonia leads to an increase of selectivity, whereas in

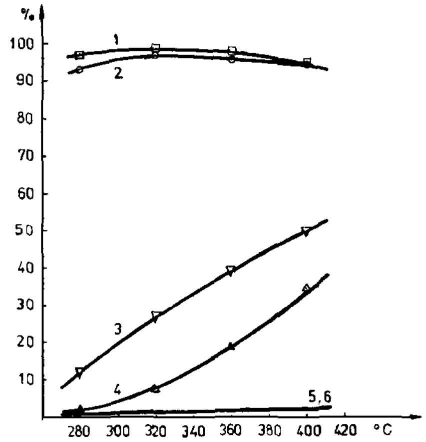

FIG. 2. Selectivity and activity to butadiene and to full oxidation in the presence (1, 3, 5) and in the absence (2, 4, 6) of ammonia for catalyst containing 0.6% thallium.

the case of a thallium content exceeding 0.3% the selectivity in the presence of ammonia is decreased. In all cases the catalytic activity in the presence of ammonia is reduced.

Thus the presence of thallium determines to a considerable extent the very high catalytic activity and selectivity of the catalysts used. The presence of thallium leads to a significant decrease of surface acidity. This is supported by the fact that addition of ammonia to the mixture has no effect on selectivity while it reduces the activity of thallium-containing catalysts. The effect of ammonia is significant in the case of catalyst containing no thallium. We observed a substantial increase in selectivity and a decrease in activity.

Kobylinski and Swift (*6*) connect the promoting effect of thallium with its large ionic radius, with a decrease of surface acidity and with the production of disorder in the crystal lattice of Al_2O_3 and MoO_3. Probably these factors are also effective in the catalysts used here.

We have observed that the addition of thallium changes the amount of oxygen from the catalyst which is able to take part in the partial oxidation of olefins.

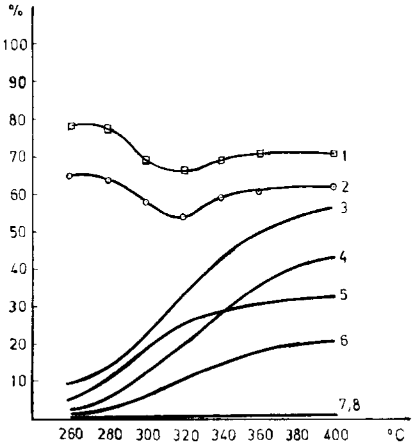

FIG. 3. Selectivity and activity to butadiene, isomerization and full oxidation in the presence (1, 3, 5, 7) and in the absence (2, 4, 6, 8) of ammonia for catalyst containing no thallium.

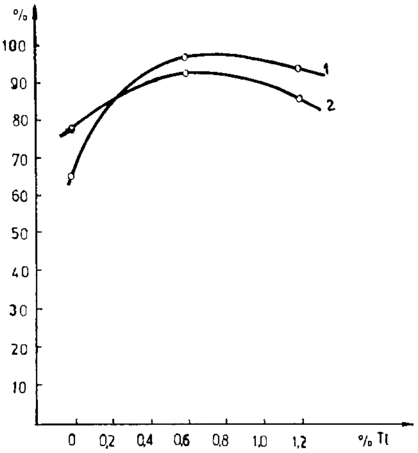

FIG. 4. Selectivity of the catalyst as a function of thallium content in the presence (1) and in the absence (2) of ammonia.

The experiments performed at 280°C employing a space velocity of butene-1 of 1550 hr^{-1} over catalysts containing 0.6% of thallium showed that the activity and selectivity displayed by the catalyst for a short time in the absence of water and oxygen were identical to those exhibited in the presence of water and oxygen. After removal of 8 monolayers of oxygen a sharp decrease in activity and change of selectivity were observed. On addition of air and steam with a ratio of 13:19 to butene the catalyst recovered its initial activity and selectivity. Since a sufficiently low temperature was chosen that the probability of coking-up is minimal, the main reason for the change in activity and selectivity is the exhausting of mobile reactive oxygen in the catalyst. Experiments analogous to those above employing catalyst containing no thallium led to analogous results. In these experiments the period of operation employing no oxygen and water was considerably shorter (equivalent to removal of 5 monolayers) compared to the case when the catalyst contained 0.6% thallium.

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