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The Catalytic Oxidative Dimerization of Propylene

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Studies have been made of the catalytic oxidation of propylene to hexadiene over thallium oxides. The reaction is selective to the 1,5-diene, the only other product being carbon dioxide which originates from the overoxidation of the hexadiene. The active component has been found to be the thallic oxide, which is reduced during the course of the reaction. Permanent deactivation of the catalyst, which occurs if thallous salts distil out of the reactor, may be avoided if sufficient oxygen is present to rapidly reoxidize the catalyst. The production of hexadiene is favored at high temperatures, although the catalyst may deactivate faster under these conditions. A reaction mechanism is proposed in which the high selectivity to the 1,5-dimer is explained in terms of the simultaneous donation of two electrons to a Tl^{3+} ion.

INTRODUCTION

In the course of an attempt to develop a catalyst for the oxidative dimerization–cyclization of propylene to benzene, thallium oxides were found to catalyze selectively the oxidative dimerization of propylene. This reaction has been previously reported only in the patent literature, in connection with lead oxide catalysts (*1*, *2*) and oxides of cadmium and thallium (*2*). Yields of straight-chain dimer of up to 70–80% based on propylene consumed have been claimed (*2*).

The reaction has advantages over conventional anionic (*3*), cationic (*4*), or Ziegler catalyzed polymerization (*5*) in that 1,5-hexadiene is produced selectively. The products of the conventional reactions tend to be branched chain molecules and, with the exception of dimers produced over anionic catalysts, to contain various numbers of monomer units.

EXPERIMENTAL

All experiments were carried out in a conventional flow system: propylene (99%, Air Products) was mixed with oxygen and nitrogen and passed over the catalyst to the analysis line. The catalyst was placed in a glass reactor which was heated in a tin bath at a temperature controlled to within ±0.1°C by a proportional controller. The analysis of the products and the remaining reactants was completed by gas chromatography using two systems. Combustible products were identified in a chromatograph fitted with a flame-ionization detector (FID) associated either with a column containing diethylene glycol–silver nitrate (30:70) supported on Chromosorb P (15 ft, 25°C) or with a column containing squalane supported on Chromosorb P (15 ft; 25°C). Noncombustible gases were analyzed with the aid of a katharometer: oxygen, nitrogen, and carbon monoxide were separated on a molecular-sieve column (3 ft; 25°C) while carbon dioxide and propylene were separated from the other components in a silica-gel column (2.5 ft; 20°C). Sampling valves were arranged so that a sample of the exit stream from the reactor could be directed either to the FID chromatograph or to the katharometer. Sample identification involved

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comparison of retention times with those of known compounds at various column temperatures and the chemical and spectroscopic analysis of the products.

The most successful catalyst was prepared by supporting the solid on fused alumina. Thallic oxide was obtained by bubbling chlorine gas through a solution of thallous nitrate and precipitating the oxide with sodium hydroxide. The precipitate was washed, mechanically mixed with fused alumina, dried overnight (150°C), and activated at 500°C in a stream of air. The catalyst contained 60% by weight of thallium oxide.

RESULTS

Preliminary studies showed that 1,5-hexadiene and carbon dioxide were the only products formed in the reaction. No conversion was observed below temperatures of ca. 350°C, and the activity of the catalyst decayed fairly rapidly, particularly in the absence of oxygen.

The effect of variation in the oxygen: propylene ratio at 500°C is shown in Fig. 1. The total flow rate and contact time were constant. The production of carbon dioxide increased, and that of hexadiene decreased with an increase in the oxygen:fuel ratio, but the total amount of products was independent of the composition of the reactant stream. No major change in the relative distribution of products was observed at shorter contact times (Table 1). In each case values were obtained over a fresh catalyst, where deactivation did not significantly affect the results.

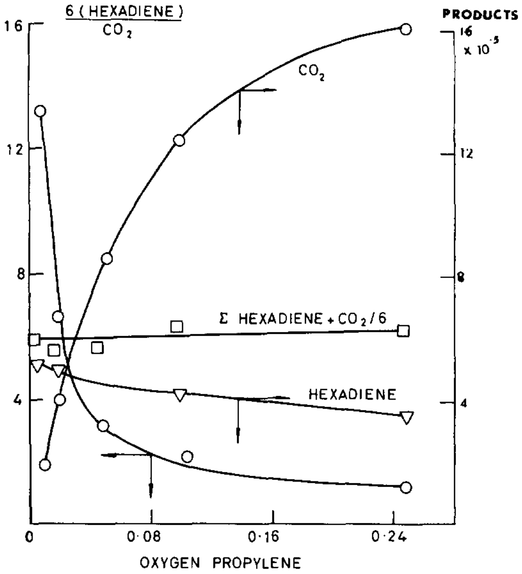


FIG. 1. The dependence of product yields on the ratio of oxygen to fuel. $T = 500$°C, contact time = 1.5 ml catalyst/ml gas/sec; Σ ({propylene} + {oxygen}) = 4.45×10^{-2} mole liter^{-1}.

The rate of deactivation of the catalyst was found to be slow at higher oxygen concentrations. Using a mixture of e.g., 1:9 oxygen:propylene, the activity and selectivity of the catalyst remained constant for comparatively long reaction times. The effect of various parameters on catalyst deactivation was checked using this reactant mixture as a standard. A freshly prepared catalyst was used first with the standard mixture, and then deactivated by passage of pure propylene for ca. 45 min. The amounts of hexadiene produced are shown in Fig. 2: Small amounts of oxygen (ca. 1%) and carbon dioxide (ca. 1%) were also produced throughout the de-

TABLE 1
THE EFFECT OF CONTACT TIME ON THE SELECTIVITY OF THE REACTION

Propylene mole/ liter × 10^{-3}	Oxygen mole/ liter × 10^{-3}	Contact time[a]	Hexadiene mole/ liter × 10^{-5}	CO_2 mole/ liter × 10^{-5}	$\frac{6 \times \text{hexadiene}}{CO_2}$
40.1	4.4	0.7	4.5	12.7	2.2
40.1	4.4	1.4	7.4	34.6	1.3
40.1	4.4	1.8	10.2	55.5	1.2
35.7	8.8	0.7	3.7	16.2	1.4
35.7	8.8	1.4	7.4	34.6	1.3
35.7	8.8	1.8	10.2	55.5	1.2

[a] Defined as vol cat./vol gas/sec.

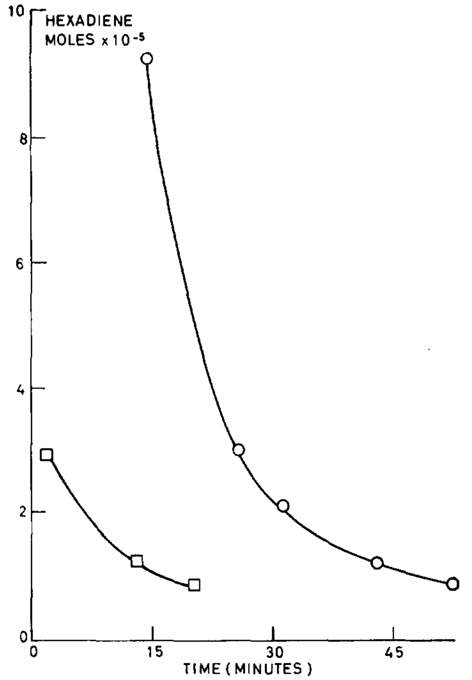


Fig. 2. Deactivation of a thallium oxide-alumina catalyst. $T = 500°$; contact time = 0.8 ml catalyst/ml gas/sec. —○—○— pure propylene; —□—□— pure propylene after preliminary deactivation by hydrogen.

activation. The catalyst was then rinsed with nitrogen and reactivated under pure oxygen for 30 min: only small amounts of carbon dioxide were produced during reactivation, and the final activity of the catalyst was the same as that of the initial solid. This deactivation–reactivation cycle could be repeated several times with no loss of "oxidized" activity, provided that no material was carried from the reactor. In one set of experiments, the oxidized catalyst was reduced with hydrogen, rinsed with nitrogen, and used with pure propylene. The results (Fig. 2) show that the activity of the catalyst was markedly reduced. No deactivation was observed when the experiments were repeated with pure nitrogen.

During these studies, it was occasionally necessary to replace the catalyst since material was being carried out of the reactor. In addition, after long usage, the glass reactor showed a yellow coloration. Analysis of the solid remaining in the reactor showed that the catalyst consisted mainly of supported thallic oxide, while the solid in the exit line consisted primarily of thallous salts. The activity of the catalyst was examined in a reactor in which it was possible to vary the free volume after the catalyst bed. The carry over of catalytic material was not associated with any pseudohomogeneous reaction.

The effect of temperature on the product spectrum was examined under conditions such that deactivation was minimized. The results shown in Fig. 3 show that the ratio of hexadiene produced to dioxide increases with temperature. The apparent activation energy for the oxidation of propylene to hexadiene can be calculated to be 52 kcal/mole compared with 21 kcal/mole for the oxidation to carbon dioxide. The distillation of catalyst from the reactor was found to

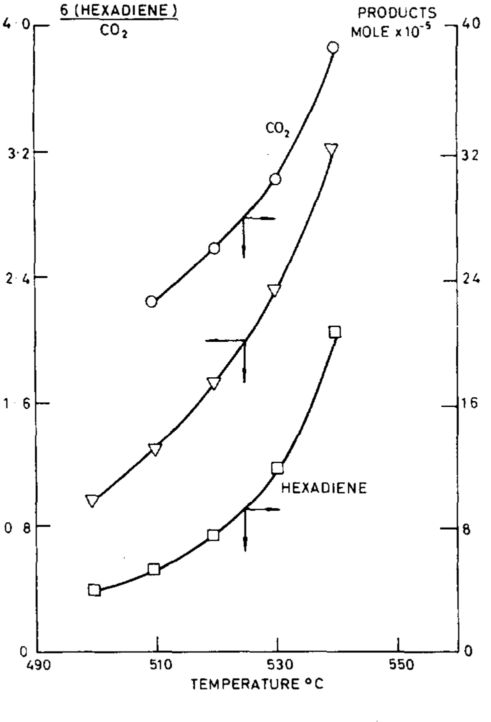


Fig. 3. The dependence of product yield on temperature Contact time = 1.5 ml catalyst/ml gas/sec. [Oxygen] = 4.45×10^{-3} mole liter^{-1}; [propylene] = 4.0×10^{-2} mole liter^{-1}.

be considerably faster at higher temperatures.

Preliminary experiments using thallium tungstate as a dimerization catalyst were completed. The catalyst was found to be much more thermally stable, but the selectivity over this solid was less.

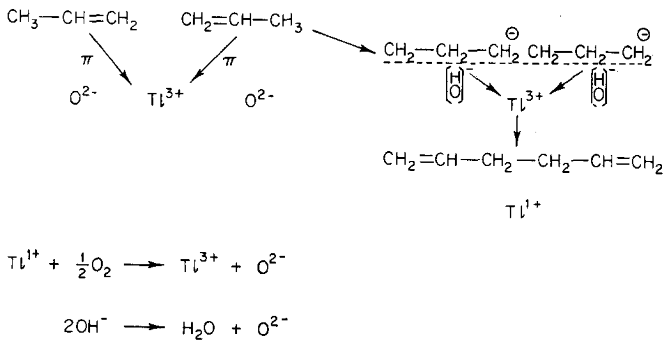
DISCUSSION

The dependence of the products of reaction upon the oxygen:fuel ratio shows that the yield of hexadiene is reduced by over-oxidation. Extrapolation of the results in Fig. 1 indicate that maximal yields should be obtained at zero concentration of oxygen. Under these conditions, however, the catalyst rapidly deactivates (Fig. 2). The deactivation is reversible but is not accompanied by significant deposition of carbon; hydrogen also deactivates the solid. It would appear that the active component of the catalyst is thallic oxide, and that this is reduced during the oxidation. Although the presence of gaseous oxygen favors over-oxidation, a certain amount must then be tolerated to ensure that the thallous salts produced in the reaction are reoxidized.

A similar conclusion emerges from consideration of the thermal instability of the catalyst. Thallic oxide fuses at 717°C and has a very low vapor pressure in the temperature range of the reaction (*6*). Thallous oxide, on the other hand, melts at 300°C and vaporizes at 506°C at atmospheric pressure. In addition, thallous salts are known to attack glass (*6*). It would appear then that the activity of the catalyst is permanently reduced if thallous salts distil out of the reactor or if thallous salts attack the glass reactor walls. Both effects would be expected to be enhanced at high temperatures and low oxygen concentrations, conditions where the decrease in activity of the catalyst is found to be particularly severe.

The optimum temperature of reaction must, then, be a compromise. The values of the activation energy are such that an increase in temperature favors the production of hexadiene, but such an increase also speeds up deactivation. An attempt to use the more thermally stable thallium tungstate was not successful in that the selectivity of the chemical reaction was less. Further experiments on thallium salts were not attempted since the development of an indium oxide catalyst (*7*) offered an alternative route to hexadiene and to benzene.

The most satisfactory reaction mechanism would seem to depend on the Tl^{3+}–Tl^{1+} redox couple. This reduction requires two electrons, effectively at the same moment. If two propylene molecules adsorb at a Tl^{3+} center (*8*), donation of two H^+ ions to the oxide, coupled with the transfer of two electrons to the Tl^{3+} center should lead to the production of species conveniently placed for straight-chain dimerization to 1,5-hexadiene.



The results obtained indicate that the reaction should be operated in a circulating system to obtain maximum selectivity. The combination of a reaction at fairly high temperatures between propylene and the oxidized catalyst with catalyst reoxidation in the absence of propylene, possibly at lower temperature, would appear to offer many advantages.

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