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Oxidative Dehydrodimerization of Propylene over a Bi_2O_3–La_2O_3 Oxide Ion-Conductive Catalyst

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The oxidative dehydrodimerization of propylene to C_3-dimers (1,5-hexadiene and benzene) has been examined at 600°C and atmospheric pressure using a $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ oxide ion-conducting catalyst in a reactor where a catalyst disk separates a feed of propylene in helium from air. The surface of the disk exposed to propylene was reoxidized not by gaseous O_2, but by the dissociative adsorption and reduction of dioxygen at the oxidant side of the disk, followed by oxide ion conduction to replace spent lattice oxygen. Selectivity to C_3-dimers when using lattice oxide migration to reoxidize the catalyst was considerably greater than when O_2 was added to the propylene feed under the same reaction conditions. This result supports the proposal that lattice oxygen is predominantly involved in the selective oxidation of propylene to C_3-dimers, and demonstrates that Bi_2O_3-based oxide ion conductors can be used as catalysts in reactions where catalyst reoxidation can occur via oxide ion conduction.

INTRODUCTION

The oxidative dehydrodimerization of propylene to 1,5-hexadiene and benzene using a variety of bismuth oxide-based catalysts has been reported (*1–10*). The reaction has been proposed to proceed through a catalyst reduction/oxidation cycle. A rate-limiting H-atom abstraction from propylene produces an allyl radical on the catalyst surface, and dimerization of two such allyl radicals (*2*) or reaction of an allyl radical with propylene (*6*) results in the formation of 1,5-hexadiene. Subsequent dehydrocyclization and aromatization of 1,5-hexadiene yields benzene. Whereas only lattice oxygen is believed to be involved in the selective oxidation of propylene to C_3-dimers, the oxidation of both propylene and C_3-dimers to carbon oxides is thought to occur through the action of both chemisorbed O_2 and lattice oxygen (*7*): in the absence of added O_2, production of carbon dioxide decreases and selectivity to C_3-dimers increases (*2*), and bismuth oxide is reduced to bismuth metal (*3, 7*).

Maximum selectivity to C_3-dimers is obtained when performing the oxidative dehydrodimerization of propylene in the absence of added O_2, but under these reaction conditions the catalyst is rapidly reduced and must be reoxidized in a separate step. An alternative to cycling between catalyst reoxidation and propylene dehydrodimerization would be to run the reaction in such a way that the catalyst could be constantly reoxidized without cofeeding O_2 with propylene or producing chemisorbed O_2 on the active catalyst surface. This principle has already been demonstrated for the oxidation of ethylene (*11*) and propylene (*12*) to the corresponding epoxides and carbon dioxide, where O_2 and hydrocarbon were separated by an oxide ion-conducting yttria-stabilized zirconia solid electrolyte coated with a porous silver catalyst film, and O^{2-} was electrochemically "pumped" through the solid electrolyte to the catalyst. Epoxide selectivity and yield increased considerably compared to the same reaction run in the presence of added O_2 and without O^{2-} "pumping." Similar applications of scandia- or yttria-stabilized zirconia which conduct O^{2-} have been demonstrated for the oxidative dehydrogenation of ethylbenzene to styrene (*13*), removal of oxygen from Pt

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and Au catalysts to significantly enhance the rate of NO decomposition (*14*), oxidation of ammonia to cogenerate NO and electricity (*15*), oxidation of SO_2 (*16*), electrooxidation of H_2, CO, and CH_4 (*17*), and removal of oxygen from nickel catalysts to increase the rate of methanation of CO or CO_2 by H_2 (*18*). Fortunately, certain mixed metal oxides based on Bi_2O_3 exist which have good ion conductivity, so that the utility of reoxidizing a catalyst for the oxidative dimerization of propylene by oxide ion conduction can be examined.

The high temperature phase (δ phase) of Bi_2O_3 exhibits a defect fluorite-type (fcc) crystal structure and is a highly conductive (ca. 1 ohm^{-1} cm^{-1}) oxide ion conductor. This phase is unstable below 730°C, where it transforms to the monoclinic phase (α phase) which is a poor oxide ion conductor but an electronic conductor (*19–22*). However, mixed oxides based upon Bi_2O_3 and containing solid solutions of di-, tri-, penta-, or hexavalent oxides are stable from ambient temperature to 800°C and exhibit oxygen ion conductivities up to an order of magnitude greater than those of the stabilized zirconias at a corresponding temperature (*23–27*). We have chosen to examine $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ (*23*) as a catalyst (in the form of a metal oxide disk) for the oxidative dehydrodimerization of propylene, where propylene and oxygen are separated by the disk and the propylene side of the disk is reoxidized not by gaseous O_2, but by the dissociative adsorption and reduction of dioxygen at the oxidant side of the disk, followed by oxide ion conduction through the disk to replace spent lattice oxygen.

METHODS

Preparation of $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ disks. To a 1-liter beaker was added 500 ml of 10% HNO_3, 300 g (0.062 mol) of $Bi(NO_3)_3 \cdot 5H_2O$, and 47.3 g (0.109 mol) of $La(NO_3)_3 \cdot 6H_2O$. This mixture was heated to 80°C with stirring until all solids had dissolved, then ca. 150 ml of concd NH_4OH was added dropwise until the pH of the solution increased from less than 1.0 to 4.0, producing a white precipitate. The resulting mixture was heated to boiling until the volume was reduced to ca. 200 ml, then dried at 110°C, calcined at 290°C for 4 h and then 425°C for 16 h, and the resulting white solid ground to a fine powder. This powder was heated in air at 800°C for 16 h, and the resulting yellow solid ground to less than 45 μm particle size, pressed into disks 2–3 mm × 13 mm diam. using a hydraulic press, and the disks again sintered in air at 800°C for 16 h. A $\frac{5}{16}$-in. end mill mounted on a drill press was used to reduce the thickness of the center of the disk to ca. 0.030 in., and then the disk center was further reduced to a thickness of 0.015–0.020 in. using wet 600-grit sandpaper.

Metal oxide disk reactor. Reactions were performed in a specially designed Inconel 601 reactor (Fig. 1). First, a Bi/La oxide disk was sealed into an Iconel "disk carrier insert" by placing a disk in a threaded insert whose internal side wall (the wall which would be in contact with the side of the disk) had been sputter-coated with silver metal and heated in air at 650°C for 15 min, and then syringing a slurry of low-melting glass composition TGC-50 (Transene Co.) in the solvent 2-butoxyethylacetate between the top edge of the disk and the silver-sputtered insert wall. The insert was then heated at 150°C for 15 min to dry the glass-slurry, then at 760°C for 15 min to melt the glass composition and seal the disk to the insert. A gold gasket, made by melting the two ends of a 0.50-mm-diameter gold wire together in a flame, was placed in the bottom of the reactor and the insert screwed down into the body of the reactor until it seated tightly against the gold gasket. The surface area of the disk exposed to the substrate (hydrocarbon) side of the reactor was 0.46 cm^2, and the volume of the substrate side of the reactor facing the disk was 0.20 cm^3. After checking the reactor for leaks by pressurizing the substrate side of the reactor to 100 psi with helium, the top of the reactor was screwed down onto a second gold gasket, the reactant and oxidant feed lines attached to the reactor, and

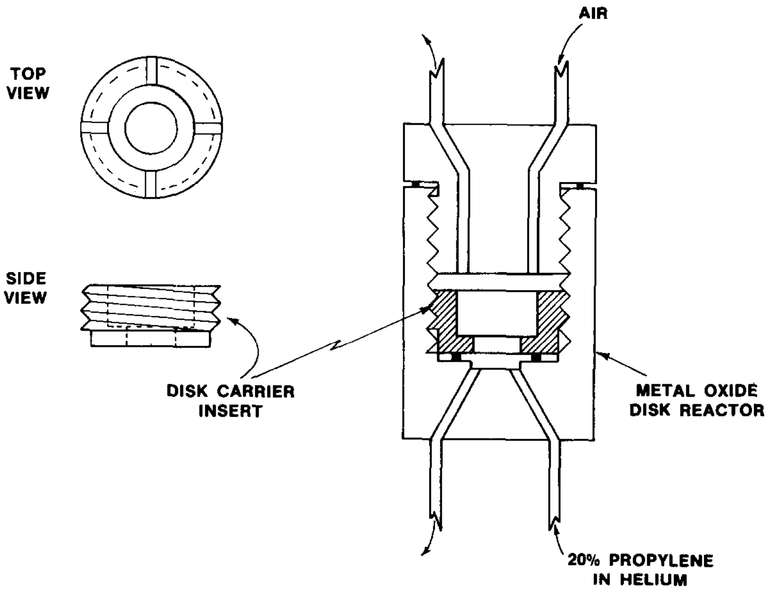

FIG. 1. Disk carrier insert and metal oxide disk reactor.

the reactor placed in a suitcase furnace. Gases were mixed and flow rates regulated using Brooks mass flow controllers. A flow rate of 2.2 ml/min through the substrate side of the reactor corresponded to a residence time of 5.5 s.

Oxidative dehydrodimerization of propylene using a $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ *disk as catalyst.* A $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ disk was sealed into the reactor described above, and a mixture of 20% propylene in helium passed through the substrate side of the reactor at atmospheric pressure and a flow rate of 2.2 ml/min while air was passed through the oxidant side of the reactor at this same pressure and flow rate. The reactor was heated to 600°C, and the reactor effluent bubbled through a toluene scrubber cooled to −78°C; this scrubber solution was analyzed for hexadienes, cyclohexadienes, and benzene using 2,2,4-trimethylpentane as internal standard on a BP-10 capillary gas chromatography column. The reactor effluent was collected prior to the scrubber when analyzing for recovered propylene, carbon monoxide, carbon dioxide, methane, and C_2-hydrocarbons by gas chromatography. Selectivities to C_3-dimers, carbon dioxide, carbon monoxide, and methane were calculated from the yields of these products and the amount of propylene reacted, after correction for moles of product produced from moles of propylene reacted (1.0 hexadiene or benzene/2.0 propylene; 3.0 CO_2, CO, or CH_4/1.0 propylene). Neither 1,3- nor 1,4-cyclohexadiene was observed as a stable reaction product under our reaction conditions. Identity of reaction products was confirmed by gas chromatography–mass spectroscopy. A blank run was also performed by substituting an Inconel plug for the disk in the reactor; under identical conditions, no reaction of propylene was observed.

Oxidative dehydrodimerization of propylene using $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ *as catalyst in a fixed-bed plug flow reactor.* $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ (0.20 g, ca. equivalent to the weight of a disk) was ground to 20–35 mesh (0.05 m^2/g) and placed between two plugs of glass wool inside a 3-mm i.d. × 21-in. quartz tube. The quartz tube was placed in a suitcase furnace, and a mixture of 20% propylene and 1% oxygen in helium was fed

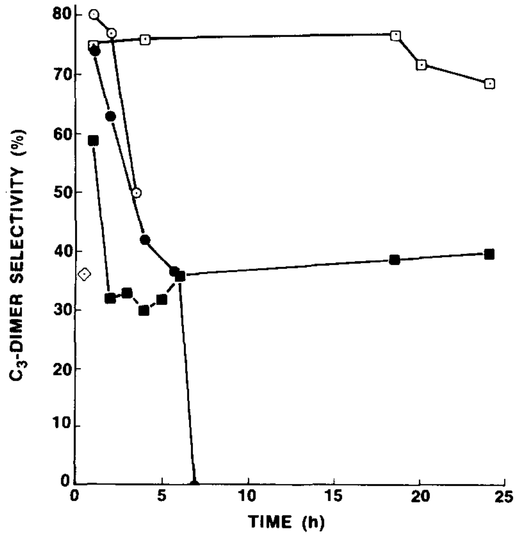

FIG. 2. C_3-dimer selectivity for the oxidative dehydrodimerization of propylene using a Bi_2O_3–La_2O_3 catalyst; catalyst disk separating propylene in helium from air and catalyst reoxidation by oxide ion conduction (⊡), disk and no catalyst reoxidation (⊙), disk and air/propylene feed (◇), 20–35 mesh catalyst in a fixed bed plug-flow reactor and catalyst reoxidation with cofed O_2 (■), catalyst in a plug-flow reactor with no catalyst reoxidation (●).

at 2.6 ml/min and atmospheric pressure over the catalyst as it was heated to 600°C (the amount of oxygen added to the feed was chosen to produce approximately the same conversion of propylene as was observed for runs performed using Bi/La oxide disks as catalyst). The reactor effluent was collected in a scrubber containing 5.0 ml of toluene and 50 μl of 2,2,4-trimethylpentane as GC internal standard and cooled to −78°C.

RESULTS

Figure 2 compares the selectivity to C_3-dimers (1,5-hexadiene and benzene) obtained for the oxidative dehydrodimerization of propylene when using $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ as catalyst in three separate reactions: (1) a catalyst disk separating 20% propylene in helium from air, and catalyst reoxidation by lattice oxide migration, (2) a catalyst disk separating a mixture of 20% propylene/1% air in helium from air, and (3) a 20–35 mesh catalyst in a fixed bed plug-flow reactor with a feed of 20% propylene/1% O_2 in helium. With air used to reoxidize the disk by replenishing lattice oxygen from the opposite side of the disk, and with no O_2 added to the 20% propylene in helium feed, a 3.2% conversion of propylene was obtained, with selectivity to C_3-dimers of 77% (53% 1,5-hexadiene, 24% benzene); during 24 h of continuous operation, CO_2 (20%), CH_4 (2%), and CO (1%) were also produced. The selectivity to C_3-dimers was relatively unchanged over a range of propylene conversion of 1–5%.

When in addition to flowing air through the oxidant side of the reactor, 1% air by volume was added to the 20% propylene in helium fed through the substrate side of the reactor, a 4.1% conversion of propylene was obtained after 0.5 h of reaction, with selectivity to C_3-dimers of 36% (12% 1,5-hexadiene, 24% benzene) and 64% CO_2. When the $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ disk was not continuously reoxidized (no O_2 was added to the propylene feed and helium was passed through the oxidant side of the reactor), an initial selectivity to C_3-dimers of 80% at 5.2% conversion after 1 h of reaction dropped to a 50% selectivity at 2.0% conversion after 4 h; the reaction stopped short thereafter as the disk was further reduced. XPS analysis of the disk after this reaction had been discontinued indicated that over half of the bismuth present was in the metallic state.

Using a 20–35 mesh $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ catalyst in a fixed bed plug-flow reactor with a feed of 20% propylene/1% O_2 in helium, the selectivity to C_3-dimers dropped from 59% (46% 1,5-hexadiene, 13% benzene) at 4.3% conversion and 1 h of reaction to 32% (21% 1,5-hexadiene, 11% benzene) at the same conversion after 2 h, after which time the selectivity to C_3-dimers remained in the range of 32–39% over the next 22 h of reaction (Fig. 2). The reaction was repeated except that no oxygen was added to the 20% propylene in helium feed, and the selectivity to C_3-dimers dropped from 74% (55% hexadiene, 19% benzene) at 3.8% conversion after 1 h of reaction to 36% selectivity (benzene only) at 0.5% conversion after 6 h. At 7 h, the conversion of propylene was only 0.3%, with CO_2, CO, and CH_4 the only observed products. Shortly thereafter, no reaction of propylene was observed as the catalyst was further reduced.

DISCUSSION

Selectivity for the production of 1,5-hexadiene and benzene from the catalytic oxidative dehydrodimerization of propylene when using lattice oxide migration to reoxidize a $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ catalyst disk (77% selectivity at 3.2% conversion) was much greater than when O_2 was added to the propylene feed (36% at 4.1% conversion) under the same reaction conditions, or when the catalyst was used in a fixed bed plug-flow configuration and oxygen was cofed with the propylene (32–39% selectivity at 4.1% conversion). The C_3-dimer selectivity using the disk setup under catalytic conditions was approximately equivalent to the initial selectivities obtained when using this same mixed-metal oxide as a stoichiometric oxidant (no catalyst reoxidation) in a fixed bed plug-flow configuration, or when the disk was not reoxidized by lattice oxygen migration. The disk rapidly became reduced and the reaction stopped if no air or oxygen was fed through the oxidant side of the disk reactor, demonstrating that lattice oxide migration was responsible for catalyst reoxidation, and that the reaction can be run in a catalytic mode without adding O_2 to the propylene feed by using this method.

The practical applications of Bi_2O_3-based oxide ion conductors are somewhat limited by the fact that these materials are purely anion conductors only at relatively high oxygen partial pressures; they are easily reduced at low oxygen potentials and become good electronic conductors (*19–21*). If the metal oxide is maintained in a highly oxidized state and is not reduced (by the oxidation of a hydrocarbon substrate) faster than oxide ion migration can replace spent lattice oxide, Bi_2O_3-based oxide catalysts can be used as a solid oxide ion-conducting electrolyte. The emf(E) generated across a solid oxide electrolyte membrane with each side maintained at a different oxygen partial pressure P_1 and P_2 is given by the Nernst relation,

$$E = ((RT/4F)\ln(P_2/P_1))t_i$$

where t_i (transport number) is a measure of the fraction of the total current carried by ions and is chosen as $t_i = 1$ for a purely ionic conducting electrolyte (*20*). P_2 and P_1 represent the partial pressure of gaseous oxygen that would be in equilibrium with oxygen on the disk surface exposed to air and propylene/helium, respectively. Because the oxygen partial pressure on the propylene/helium side of the disk (P_1) could not be accurately measured under reaction conditions, an approximation of P_1 was made by measuring the oxygen concentration in the He feed when He and air were passed separately past the two faces of the disk at the same reaction temperature. This approximation represents an upper limit of the partial pressure of oxygen on the propylene/helium side of the disk under reaction conditions, and calculation of E using this approximation produces an estimate of the lower limit of the emf across the disk. Assuming that P_2/P_1 in our system is ca. 2.1×10^2 ($P_2 = 0.21$ atm, $P_1 \simeq 0.001$ atm), the emf across the disk at 600°C is calculated to be 0.10 V. The resistance (R) across the disk can be calculated from the disk geometry and the previously reported conductivity of $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ at 600°C ($\sigma = 0.1$ ohm^{-1} cm^{-1}) (*23*) from

$$R = (L/A)\sigma^{-1}$$

and the rate of O_2 transport (G_{Ox}) across the catalyst approximated from $i = E/R$ and $G_{Ox} = i/4F$. The rate of O_2 transport across the metal oxide disk is therefore approximately 2.6×10^{-7} mol/s, while O_2 is used to produce 1,5-hexadiene, benzene, and CO_2 at a rate of 3.2×10^{-8} mol/s (i.e., ca. 12% of the calculated O_2 flux). The actual O_2 flux across the disk may be less than calculated due to grain boundary effects, a lower conductivity (σ) than has been reported for the $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ disk which we employed, and/or a $t_i < 1$. The Bi_2O_3-based metal oxide disk was able to function as a solid oxide ion conductor and catalyst for the oxidative dehydrodimerization of propylene because the oxide was most likely not significantly reduced under the described reaction conditions.

CONCLUSIONS

The ability to use a $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ as an oxide conductor and catalyst for the oxidative dehydrodimerization of propylene to 1,5-hexadiene and benzene has been demonstrated. A considerable increase in selectivity to C_3-dimers was observed when the catalyst was continuously reoxidized by lattice oxide migration as compared to running the reaction with oxygen present in the hydrocarbon feed for catalyst reoxidation. Overreduction of the catalyst disk and loss of catalyst activity was not observed as long as the rate of propylene oxidation was less than the rate of oxide ion conduction across the disk. This method of selective oxidation using Bi_2O_3-based oxide ion conductors instead of scandia- or yttria-stabilized zirconia conductors has the advantage that oxide ion conductivities of Bi_2O_3-based conductors are significantly greater at a given temperature, and that the oxide ion conductor can also function as the catalyst.

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