Oxidation of Propylene

Direct Synthesis of Propylene Oxide with CO_2 as the Solvent

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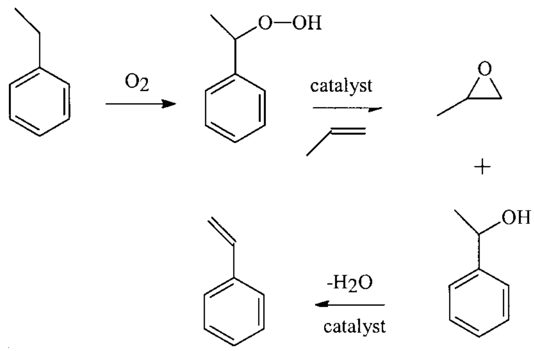
Over four million tons of propylene oxide (PO) are produced worldwide each year by either chlorohydrin or coproduct processes.[1] While these are well-established processes, they produce PO by indirect routes and therefore require substantial amounts of raw materials and energy as well as high capital investment. In the chlorohydrin route to PO, propylene is treated with chlorine to produce 1-chloro-2-propanol (and HCl), which is then treated with base to generate PO and salt. In this process approximately two pounds of salt waste are produced per pound of product, which leads to production of wastewater at volumes roughly 40 times that of the PO produced.

Hydroperoxide-based processes generate PO and a coproduct, either styrene or isobutylene. The process with styrene as the coproduct (Scheme 1) now predominates, although this route requires five major reaction steps to produce PO and recover the styrene coproduct. The high capital requirement of this process for producing PO is partially offset by the production of styrene, yet current PO producers have been searching for some time for alternatives.



Scheme 1. Hydroperoxide process for generation of PO with styrene as the coproduct.

Direct oxidation of propylene to PO with O_2 would be highly desirable,[2] but as propylene with its allylic hydrogen atoms is highly combustible, this is quite difficult.[3,4] Researchers have shown[5] that a titanium silicalite (TS-1) catalyst promotes the formation of PO from propylene and H_2O_2 at selectivities approaching 100%. Because H_2O_2 is an environmentally benign oxidant, this route would seem to combine both green and economic advantages. Unfortunately, premanufactured H_2O_2 is currently too expensive to allow an economically viable process.[6] What if H_2O_2 could be generated in situ from hydrogen and oxygen? Holderich and colleagues[7] have examined the liquid-phase generation of PO from hydrogen, oxygen, and propylene in methanol/water over Pd (alone and with Pt) on TS-1. Inclusion of promoters (such as NaBr) resulted in conversion and selectivity of 40% in batch experiments. Semicontinuous runs increased the selectivity to over 60% while the conversion dropped substantially.

The use of TS-1 to generate propylene oxide from propylene and hydrogen peroxide (either premanufactured or generated in situ) has been investigated extensively over the past decade. In general researchers have concluded that an alcohol (preferably methanol) is needed as part of the solvent mixture to perform the reaction efficiently. Clerici and colleagues, for example, propose that methanol interacts with the catalyst surface at the active site.[8] Other researchers[5b,7a,9] confirm Clerici's contention that the highest activities in traditional solvent systems are obtained with methanol as the sole solvent or as the cosolvent with water.

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Jenzer et al. have recently investigated the generation of PO from H_2, O_2, and propylene over a Pt/Pd/TS-1 catalyst in a continuous fixed-bed reactor[10] with a mixture of methanol and water as the solvent. Byproduct generation was extensive, where the primary byproduct was methyl formate (acetone, acrolein, acrylic acid, and PO ring-opening products were also observed). The formates were formed by the oxidation of methanol, a known reaction that takes place under mild conditions. Hydrolysis followed by further oxidation creates formic acid, which then reacts with methanol to generate the formate.

In summary, the literature suggests that methanol is needed for efficient epoxidation, yet the methanol/water solvent is also the major source of the byproducts. The presence of the liquid solvent also creates certain process problems. The rate of the reaction is most likely limited by the diffusion of the gaseous reactants across the vapor–liquid interface. Water is a benign and safe solvent, yet the solubility of the gases (H_2, O_2, and propylene) in water is low, which creates a potential mass transfer problem. The addition of methanol improves the solubility of the gases in the liquid phase, yet reactions with methanol are a prime source for byproducts.

Given this background, we have investigated the use of carbon dioxide as the sole solvent for the generation of PO from hydrogen, oxygen, and propylene over a Pd/TS-1 catalyst. We wished to determine whether we could reap the benefits of CO_2 use (vide infra) while avoiding the problems of by-products arising from methanol. Given the results of Clerici et al.[8] and of others,[5b,7a,8,9] a key question was whether the reaction would proceed effectively in the absence of methanol. We have previously shown that one can generate H_2O_2 in CO_2 from O_2 and H_2 and that liquid CO_2 is a safe solvent that will not form oxidation byproducts.[11] Further, the chemistry could proceed without the transport limitations across liquid and gas phases. CO_2 provides a unique combination of advantages to this process: it can solubilize large quantities of gases, is immune to oxidative degradation, provides a nonflammable environment in which to mix H_2 and O_2, and is miscible with both propylene and PO. The use of CO_2 as a safe, benign solvent in oxidations has gained increasing interest in the research community over the past five years.[12]

The effect of the solvent system (CO_2 versus water/MeOH) was compared in three sets of experiments, in which a) CO_2 served as the sole solvent, b) a methanol/water solvent system was employed with nitrogen at the same operating pressure as in a), and c) a methanol/water solvent system was used with CO_2 at the same operating pressure as in a). The results are reported as the conversion of propylene and selectivity of the oxidation to PO (total PO divided by total amount of propylene in the products detected) at the conclusion of the 4.5-h runs.

Table 1: Results for batch epoxidation of propylene in three different systems.[a]

Solvent system	Catalyst mass [g]	Propylene conversion [%]	Propylene selectivity to PO [%]	C_3H_8 [%]	ring-opened byproducts [%]
CO_2	0.1502	9.5	77.1	22.9	–[b]
CO_2	0.1952	6.5	91.2	8.8	–[b]
CO_2	0.2998	7.5	94.3	5.7	–[b]
$MeOH + H_2O + CO_2$	0.1565	3.5	17.4	75.0	7.6
$MeOH + H_2O + CO_2$	0.2063	4.7	41.1	46.5	12.4
$MeOH + H_2O + N_2$	0.1993	16	3.5	95.2	1.4

[a] Total pressure = 13.1 MPa, $T = 318$ K, 4.5 h reaction time. In all cases the absolute concentrations were 4 mM for propylene, 1.26 mM for H_2, and 8.3 mM for O_2, in 3.84×10^{-5} m^3 CO_2. Conversion continued to change up to 4.5 h, so we believe that the hydrogen had not yet been completely consumed at that point. [b] No PO ring-opened byproducts (propylene glycols, methoxypropanols, or propylene carbonate) were detected by online GC analysis.

As shown in Table 1, the use of CO_2 as the sole solvent in the reaction allows high selectivity to PO at reasonable conversions, whereas selectivity drops when methanol/water is added. The latter results are consistent with Jenzer's observations that methanol is a major contributor to byproduct formation (both through reaction with PO and oxidation), and that use of CO_2 in place of nitrogen leads to improvements. Additional byproducts observed when methanol was present include methyl formate, 1-methoxypropan-2-ol, and 2-methoxypropan-1-ol. Typically, the molar ratio of these three was 12:1.7:1, in agreement with previous observations that methyl formate is the major byproduct when methanol is present.

From entries 1–3 in Table 1, it would appear that simply increasing the amount of catalyst in the reactor increases the selectivity of the reaction, but this is somewhat deceiving. We strongly suspect that, although the catalyst was pretreated with hydrogen before the experiment, the first step in the process in the reactor is additional reduction of the catalyst by available hydrogen, which then changes the hydrogen:oxygen ratio (from a molar perspective, the amounts of palladium and hydrogen are indeed comparable at higher levels of catalyst). It is known that lowering the hydrogen:oxygen ratio favors the formation of H_2O_2 rather than H_2O over palladium. Further, the reduction in the amount of available hydrogen lessens the chances for simple hydrogenation of propylene to propane.

The presence of the gas–liquid interface (entries 3—6, Table 1) also contributes to decreasing selectivity, as any splashing of the powder catalyst onto the walls of the reactor would lead to the gas-phase hydrogenation of propylene. The last two entries in Table 1 show that use of nitrogen as the pressure-transmitting medium leads to enhanced conversion but low selectivity as the significant gas–liquid interface promotes propane formation. (It is also possible that methanol can further reduce the palladium to the point where hydrogenation of propylene is favored over production of hydrogen peroxide.) The fact that the conversion and selectivity were better with CO_2 and MeOH/water than with N_2 and MeOH/water can be explained by phase-behavior effects. CO_2 will swell a mixture of methanol/water (3/1), and hence improvements owing to the replacement of nitrogen by CO_2 may arise from increased solubility of the gaseous reactants (O_2, H_2 and propylene) in the liquid phase due to the presence of CO_2. Also, a mixture of N_2, propylene, O_2, H_2 and MeOH/water will likely create a three-phase mixture, while use of CO_2 (in place of N_2) will likely create a two-phase mixture, which thus reduces the number of interfaces and enhances transport. When CO_2 is employed as the sole solvent, the gas–liquid interface is eliminated entirely, further enhancing selectivity.

Since we conducted our experiments in batch mode with relatively small amounts of H_2 and O_2, we were not fully able to gauge the effect of the MeOH/water solvent vs. CO_2 on the formation of PO ring-opened products. Consequently, control experiments were conducted in which catalyst, PO, water (only the relatively small amount of water that would be expected to be produced with the PO), and CO_2 (13.1 MPa, 318 K) were added to the reactor. After 4.5 h only 4.5 % of the PO was converted to ring-opening products (i.e. propylene glycol). The analogous experiment conducted with the MeOH/water solvent system and N_2 resulted in 60 % conversion of PO to methoxypropanols. These results can be accounted for in large part by the fact that with CO_2 as the sole solvent there is a much lower concentration of hydroxy-containing compounds that can react with PO.

In summary, we have found that carbon dioxide is an excellent solvent for the epoxidation of propylene, where the in situ reaction of H_2 and O_2 creates the oxidant. Unlike organic solvents, CO_2 can solubilize large quantities of gases, is immune to oxidative degradation, provides a nonflammable environment in which to mix H_2 and O_2, is miscible with both propylene and PO, and is chemically inert to the PO product. Significantly, we have found that methanol is not required for the efficient production of PO from propylene and H_2O_2 produced in situ, contrary to suggestions from previous reports.

Experimental Section

The catalyst was prepared by suspending TS-1 (1.6 % Ti, 20 g) in deionized water (8.0×10^{-5} m^3) in the presence of tetraamine palladium nitrate (5 % Pd, 2.542 g) at 353 K for 24 h. The solid was recovered by filtration under pressurized N_2, washed with deionized water, dried under vacuum at 323 K, and then calcined at 423 K for 4 h in 5 % O_2/95 % N_2. The resulting catalyst has 0.47 % Pd by weight. Pd/TS-1 catalyst prepared in this way was then suspended in methanol/water (3/1; 2 g catalyst in 100 mL solvent) and preactivated in a 1×10^{-4} m^{3}min^{-1} gas flow (10 % propylene, 4 % O_2, and 4 % H_2) at 318 K and 0.02 MPa for 22 h.

Reactions were carried out in a 4×10^{-5} m^3 stainless steel batch reactor capable of operating pressures to 40.0 MPa at temperatures up to 373 K. The contents were mixed with a multiblade stirrer (Parr Instrument Co) that had been mated to the reactor lid. Gases were introduced with a calibrated high-pressure syringe pump (High Pressure Equipment Co, Erie, PA). The temperature of the reactor was monitored with a thermocouple fitted through one of the five reactor ports, while the pressure was monitored with a transducer and readout. Samples could be withdrawn from either liquid or gas phases through an additional pair of ports, each fitted with a frit filter to retain catalyst. Material was injected through the final two ports. Samples were analyzed by GC (Hewlett Packard 5890 Series 2, with either a TCD or FID detector). Where CO_2 alone was the solvent, the reactor was charged with a known amount of catalyst, and then evacuated. The reactor was heated to 318 K and known amounts of CO_2, hydrogen, O_2/N_2, and propylene were added in that order. Additional CO_2 was added by using the compressor (Haskell Equipment Co, Houston) to achieve a final pressure of 13.1 MPa. The mixture was mixed vigorously, sampled at intervals for GC analysis, and then slowly depressurized to 1 atm. Any side products that precipitated on the catalyst were extracted in methanol and analyzed separately by GC. When methanol/water was employed as the solvent, methanol/water (3/1; 1.0×10^{-5} m^3) was added to the reactor with the catalyst before the experiment. Both the gas and liquid phases were sampled and analyzed for PO and other products. For some of the two-phase (gas–liquid) experiments, N_2 was substituted for CO_2.

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