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A general integrated process for synthesizing olefin oxides

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Metal oxide solid reactants are shown to react with vicinal alkyl dibromides to selectively form olefin oxides and fully regenerable metal bromides.

Epoxidations of olefins, especially ethylene and propylene, have long been of major industrial importance and academic interest.[1] In the absence of allylic hydrogen atoms, olefins including ethylene and styrene react with molecular oxygen on Ag-based catalysts to form epoxides.[2] More delicate means are required for allylic olefins. Propylene oxide (PO), for example, is produced by the relatively inefficient chlorohydrin and Halcon routes. The chlorohydrin route consumes stoichiometric Cl_2 while for the Halcon method, autoxidation of coreductants ethylbenzene or isobutane is required to form reactive hydroperoxides. Oxygen transfer from the hydroperoxides to propylene gives the epoxide as well as stoichiometric styrene or t-butanol coproducts.[3]

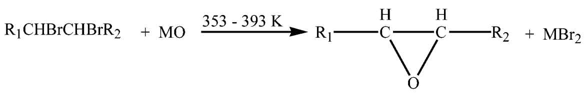
For large scale oxidation processes, oxidation with molecular oxygen is desirable from an environmental and economic perspective. Although a number of epoxidation processes exist that use a variety of catalysts and oxidants, olefin epoxidation with molecular oxygen has been successfully implemented only for ethylene oxide production. Propylene oxidation with molecular oxygen over Ag catalysts similar to those used for ethylene epoxidation leads to propene oxide selectivities of less than 15% at less than 15% conversion.[3]

The claims of recent patents of high PO selectivities in propylene oxidations over novel supported precious metal catalysts show promise, but the yields are generally low.[4] While new heterogeneous processes using H_2O_2 as the oxidant are under development that show high epoxide selectivity,[5] the cost and safety challenges of using H_2O_2 remain formidable.

We have previously demonstrated a low temperature bromine mediated process for selective alkane partial oxidation involving solid metal oxides that perform oxide/bromide metathesis during reaction, giving metal bromide solids and partial oxidation products. Regeneration of the metal bromides with oxygen allows complete bromine recovery.[6] We have extended this previous work to new metal oxide solid reactants and demonstrated epoxidation of alkyl dibromides.

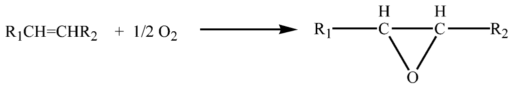
The solid reactant process implemented for the production of PO (for $R_1 = H$, $R_2 = CH_3$) is illustrated in Equations 1–4. The first step is the bromination of alkene to the alkyl dibromide. The dibromide is then reacted with the metal oxide to generate the epoxide product and metal bromide. Finally, oxygenation of the spent solid regenerates the metal oxide and Br_2 for reuse. Thus, the overall transformation of alkene to epoxide utilizes molecular oxygen as the ultimate oxidant.1

$$R_1CH{=}CHR_2 + Br_2 \xrightarrow{393\text{ - }473\text{ K}} R_1CHBrCHBrR_2 \qquad (1)$$



(2)

$$MBr_2 + 1/2\ O_2 \xrightarrow{573\text{ - }773\text{ K}} MO + Br_2 \qquad (3)$$



(4)

While others have considered related approaches,[7] we describe here the integration of these steps into a continuous process which has potential for commercialization. Furthermore, preliminary data have demonstrated that i) the product distribution can be controlled by the metal oxide composition and reaction conditions, and ii) the process can be generally applied to other alkyl dihalides including dibromoethane. Thus, both ethylene oxide and propylene oxide are produced by the same basic process.

Experimentally, the sequential reactor consists of two sections with independent temperature control. In the first, a stream of Br_2 and excess alkene reacts at T_1 (393–473 K, hot enough to keep all reagents gaseous). The Br_2 is completely consumed and the resulting vicinal dibromide(s) and excess alkene proceed to the second reactor, a fixed bed or liquid phase slurry bed reactor containg metal oxide at T_2 (353–393 K). The products exiting this reactor were analyzed by ^{1}H-NMR and gas chromatography (MS, TCD or FID detector). If the second reactor section is a fixed bed, the bed may be regenerated with O_2 at T_3 (573–773 K depending on the specific metal oxide composition) to regenerate the metal oxide and recover Br_2. If the metal oxide mixtures include redox active metals such as Cu, bromine recovery is facilitated and proceeds at lower temperature. Repetitive runs with regenerated metal oxide showed no loss of activity through multiple regeneration cycles.

Reaction of a representative metal oxide, MgO, with 1,2-dibromoethane is shown in Fig. 1.† The reaction was carried out in a 10 ml slurry semi-batch glass reactor heated by an Al block with a temperature controller. Equimolar metal oxide and 1,2-dibromoethane (5 mmol) and 3 ml water were added to the reactor with vigorous stirring and the mixture heated to 353 K and continuously purged with He at 5 sccm. Both the gas and liquid were sampled and analyzed for products by gas chromatography. The ethylene oxide and vinyl bromide selectivities were 89.5% and 10.0%. Trace CO_2 and ethylene were also detected. When the reaction was

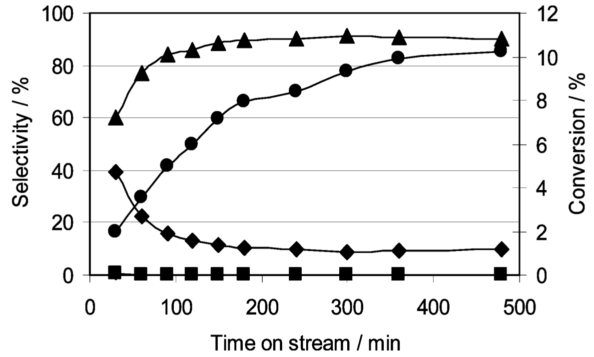


Fig. 1 1,2-Dibromoethane epoxidation by ring closing substitution using MgO as reactant. The reaction conditions were as follows: to prevent metal oxide induced degradation of the volatile PO product, He (5 sccm) was passed through a refluxing stirred reactive slurry (353 K, 298 K headspace) of MgO (0.15 g, diam. = 3 nm, 600 m^2 g^{-1}), 1,2-dibromoethane (0.5 g), and H_2O (3 g) and the volatiles collected in a Tedlar bag containing C_2H_6 internal standard. Shown are dibromoethane conversion (circles, right axis) and selectivities (left axis) to ethylene oxide (solid triangles), CO_2 (squares) and vinyl bromide (diamonds).

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Table 1 Conversions and product selectivities for reaction of 1,2-dibromopropane with metal oxides at 353 K

Metal oxides	PO Sel. (%)	Propanal Sel. (%)	Acetone Sel. (%)	2-Bromo-1-propene Sel. (%)	1-Bromo-1-propene Sel. (%)	Propene Sel. (%)	CO_2 Sel. (%)[d]	Conversion (%)
MgO[a]	17.7	ND	4.2	33.5	41.7	ND	2.9	7.0
Ag_2O[a]	75.4	2.5	6.3	8.6	5.7	1.5	ND	7.1
Ag_2O[b]	42.7	ND	ND	3.3	15.2	0.3	38.5	17.2
Ag_2O[c]	43.3	ND	ND	2.6	15.9	0.4	37.8	16.8
$YBa_2Cu_3O_7$[a]	63.5	ND	1.3	13.6	19.1	trace	2.5	10.1
$Fe_4ZnZr_5O_x$[a]	27.7	2.0	1.7	28.0	40.6	ND	ND	8.9
$Cu_4NaZr_5O_x$[a]	18.7	ND	15.6	27.9	32.4	trace	5.4	7.3

[a] Semi-batch slurry reactor, conditions identical to those in Fig. 1, except reaction time = 3 h. [b] Fixed-bed gas reactor: 10 mmol Ag_2O, 1,2-dibromopropane flow = 1.5 mmol h^{-1}, N_2 flow = 5 sccm, space time = 15 s, reaction time = 3 h. [c] Sequential zone flow reactor, T_1 = 473 K, propene/Br_2 flow = 5/0.5 sccm, 10 mmol Ag_2O, reaction time = 3 h. [d] For semibatch reactions, CO_2 was determined by GC after treatment of the spent solid with H_2SO_4 (1.0 M) in a calibrated headspace.

carried out in a fixed-bed reactor (conditions described in Table 1), the CO_2, ethylene oxide and vinyl bromide selectivity were 13.2, 16.2 and 69.7% respectively. This selectivity difference demonstrates the importance of the role of solvent or medium in determining the oxide/bromide metathesis reactivity; HBr elimination to vinyl bromide is minimized in the solution reaction. Displacement of EO from the reactive surface by other reagents in the liquid phase may also prevent further oxidation to CO_2.

The results of epoxidation of 1,2-dibromopropane over several metal oxides are shown in Table 1. Accounting for differences in conversion, propylene oxide selectivities for the slurry phase and fixed bed reactors are comparable. When the reaction was carried out in a sequential zone flow reactor in which propylene is first brominated at 473 K (propylene : Br_2 = 10 here for flow, but in principle this reaction could be quantitative) the selectivities of products are similar to those observed using 1,2-dibromopropane as reactant, confirming that the intergrated process is feasible as described in Equations 1–4. Olefin bromination at moderate temperature gives high yields of vicinal dibromides.[8] We were also surprised to find that the propane dibromination product distribution is tunable between > 90% 2,2-dibromopropane to > 90% 1,2-dibromopropane, depending on the identity of the bed material.[9] Both $MgBr_2$ and AgBr are difficult to regenerate in O_2 and require temperatures in excess of 773 K. However, several more easily regenerated metal oxides, also active for oxide/bromide metathesis of 1,2-dibromopropane to PO, have been found, including $YBa_2Cu_3O_7$, $Cu_4NaZr_5O_x$, and $Fe_4ZnZr_5O_x$.

In summary, a general solid reactant approach for olefin or alkane epoxidation using molecular oxygen as oxidant is described. Control of the product distribution by choice of the solid metal oxide composition allows conversion of vicinal dibromide intermediates to epoxides or ketones or to vinyl bromides. In addition, the vicinal dibromides can be produced by direct bromination of alkanes, or by vinyl bromide hydrobromination, providing a means of producing epoxides more directly from alkane feedstocks. Further studies are focused on improving overall conversion and epoxide selectivity as well as understanding both the metathesis and metal oxide regeneration steps with an eye toward lowering the temperature required for both steps to improve overall yield and selectivity.

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Notes and references

† MgO was purchased from NanoScale Materials, Inc. NanoActive™ Plus grade. Ag_2O was from Alfa Aesar. General metal oxides were synthesized by sol-gel techniques.[7] 100% conversion was defined by the starting amount of limiting reactant, *i.e.* 1,2-dibromopropane in most cases, or Br_2 for the reaction utilizing propene bromination as the first step.

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