CATALYTIC IMMOBILIZED IONIC LIQUID MEMBRANES

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ABSTRACT

Supported ionic liquid membranes (SILMs) were employed as membrane reactors to examine the oligomerization of ethene with and without the presence of a Ni(II) dimerization catalyst. The SILMs were prepared by imbibing either an 1.1:1.0 AlCl 3 :EMIC acidic melt or a 1.1:1.0:0.1 AlCl 3 :EMIC:MCI (MCI = LiCl, NaCl, or KCl) neutral buffered melt into a porous polyethersulfone support membranes. For SILMs without the Ni(II) catalyst, ethene oligomerization was promoted by the presence of protonic species in the neat melts, and hydrocarbon fractions from C 3 to C 6 were quantified in the product mixtures. The oligomerization activities decreased in the order acidic > LiCl buffered > NaCl buffered > KCl buffered. Importantly, the neutral buffered melts produced only saturated alkanes, while the acidic melt produced olefinic products. With the Ni(II) homogeneous catalyst added, the acidic SILM produced primarily a butene fraction, while the NaCl neutral buffered SILM yielded ethane, C 3 , and C 4 hydrocarbon fractions.

INTRODUCTION

Supported liquid membranes (SLMs) consist of a liquid supported within the pores of a thin porous support such that the liquid seals the pores of the support material and acts as a permeable medium for separation processes. 1,2 For SLMs used in gas separations, the liquid medium can be lost from the porous support matrix by evaporation or by the presence of a large pressure gradient that forces the liquid from the porous support matrix. 2 The latter problem is mitigated by capillary forces if proper wetting of the support material by the liquid is achieved, while several methods have been employed to control evaporative losses, including presaturation of the feed and permeate gas streams and the use of ion exchange membranes to retain charged carrier species. 2 A lesser known method for eliminating liquid evaporation is to utilize nonvolatile ionic liquids, or molten salts, as the liquid medium. 3-5 Such supported ionic liquid membranes (SILMs) have been
demonstrated with high temperature and room temperature ionic liquids - representative systems include molten alkali metal nitrates for oxygen recovery from an O2/N2 stream3,5 and room temperature (hexyl)4N(benzoate) for CO2 separation from CH4.4

If the ionic liquid itself, or a chemical species added to the ionic liquid, catalyzes a desired chemical reaction, then an SILM can be used as a membrane reactor. In such applications, the reactant is supplied to the feed side of the membrane and is converted to the desired product as it passes through the ionic liquid phase to the permeate side. The advantages of catalytic membranes over conventional solution phase batch reactors include (1) reduction in costly product-reactant separation steps, e.g., distillation; (2) elimination of catalyst recovery steps; (3) control of reaction time by varying the membrane thickness; (4) utilization of multiple membranes in series to carry out successive reaction steps in a single reactor; and (5) minimization of liquid needed for the reaction phase. In addition to these practical advantages, membrane reactors operate under steady-state mass transport and reaction conditions and are ideal for the simultaneous determination of reaction kinetics and permeability coefficients, i.e., product throughput.

It is important to point out that the use of supported ionic liquids as media for homogeneous catalysis is not new. Such systems were described over two decades ago by Rony and Roth,6 while Datta and coworkers have expanded substantially on this theme over the last decade7 and have recently applied these principles to a fuel cell catalytic reactor.8 In addition, the commercial production of sulfuric acid via the oxidation of SO2 relies on a supported vanadium oxide molten salt catalyst.9 Furthermore, room temperature ionic liquids have been examined as media for bulk phase homogeneous catalysis by a number of researchers,10 including recent studies by groups in Europe.11 In our own laboratories, we have demonstrated homogeneous and heterogeneous catalytic hydrogenation using SILMs containing perfluoroanion room temperature ionic liquids.12,13

Chloroaluminate room-temperature ionic liquids are known to be inherent acid catalysts for the oligomerization of ethene to a mixture of unsaturated and saturated C3 - C6 fractions.14 In melts containing no intentionally added catalytic species, oligomerization results from the presence of superacidic protonic impurities in the neat acid melts. By adding a Ni(II) catalyst with an alkylaluminum cocatalyst, the olefin oligomerization can be limited primarily to dimerization products, e.g., butene for an ethene feed. In addition, acidic melts which have been “neutralized” with an alkali metal chloride (termed neutral buffered) retain a "latent acidity"16,17 and may still promote olefin oligomerization reactions. Therefore, we decided to employ SILMs to examine the oligomerization of ethene in acidic and neutral buffered chloroaluminate ionic liquids with and without added a Ni(II)-alkylaluminum catalyst.

EXPERIMENTAL

The chloroaluminate melts were prepared as previously described.18 The membrane reactor was a Gelman 47-mm inline filter holder fitted with Swagelock® Quick-
Connect couplings. This filter holder uses an o-ring sealing mechanism and has an active membrane area of 12.6 cm$^2$. Gelman Supor®-450 polymer filter membranes (hydrophilic polyethersulfone filter material with thickness = 152 μm, pore size = 0.45 μm) were found to be stable towards the acidic and neutral buffered chloroaluminate melts and were used as the porous support matrix. The SILMs were prepared inside an argon-filled Vacuum Atmosphere glove box. Several drops of the desired ionic liquid were dripped onto the support membrane and brushed lightly with the edge of a microscope slide. The melts readily wetted the polymer support, filling the pores of the filter membrane to produce a translucent appearance. The resulting SILM was sealed in the filter holder which was then transferred to a specialized gas manifold for testing.

During catalyst experiments, the feed side of the membrane was held static at 1 atm of ethene, while the permeate side was constantly swept with a flow (nominally 5 cm$^3$ min$^{-1}$) of He for olefin dimerizations/oligomerizations. The permeate gases were vented through a manual Valco zero volume, 8-port sampling valve which was used to inject 1 mL samples of the product gases directly into the carrier gas stream of a Buck Scientific Model 610 gas chromatograph (HayeSep-Q column; TCD detector) controlled with the Peaksimple software program. From a summation of all the hydrocarbon peaks, the permeability coefficient for ethene in the acidic and neutral buffered chloroaluminate SILMs was estimated to be 130 barrers.

RESULTS AND DISCUSSIONS

Oligomerization of Ethene in Acidic 1.1:1.0 AlCl$_3$:EMIC and Neutral Buffered 1.1:1.0:0.1 AlCl$_3$:EMIC:MCl (MCl = LiCl, NaCl, KCl)

Neat 1.1:1.0 AlCl$_3$:EMIC and 1.1:1.0:0.1 AlCl$_3$:EMIC:MCl (MCl = LiCl, NaCl, KCl) were evaluated as ethene oligomerization catalysts in SILM configurations. The chloroaluminate SILMs were prepared and tested as described above. Figure 1 shows the GC detector response for the hydrocarbon fractions in the product stream as a function of time. Only the acidic melt produced a significant C$_4$ fraction, which decreased substantially after 2 hours. In fact, all hydrocarbon fractions other than C$_3$ decreased over time. Because acid catalyzed ethene oligomerization should lead to olefinic hydrocarbons containing only even numbers of carbon atoms, the C$_3$ and C$_5$ fractions observed in the product stream were produced by cracking reactions. Additionally, from the GC retention times, it was determined that the neutral buffered melts produced only alkane fractions, while the acidic melt produced olefinic products. The saturated hydrocarbons found for the neutral buffered melt were most likely produced by cracking reactions as well.

Based on the above observations, we propose that the initial activities for ethene oligomerization of the acidic and neutral buffered melts result from the presence of protonic impurities. It is noteworthy that the oligomerization activities track with the measured Brønsted acidities of the melts, i.e., acidic > LiCl buffered > NaCl buffered >
KCl buffered.\textsuperscript{16} During SILM operation, the volatile protonic impurities are purged from the thin membrane as HCl, and the ionic liquid gradually loses activity for ethene oligomerization. The increase in C\textsubscript{3} at longer times implies that this hydrocarbon fraction may result from Lewis acid promoted cracking of ethene. Finally, the neutral buffered melts appear to promote cracking more so than the acidic melt, as evidenced by the predominance of saturated hydrocarbons and the large quantities of C\textsubscript{3} in the product mixtures from the neutral buffered SILMs.

Nickel(II) Catalyzed Oligomerization of Ethene in Acidic 1.1:1.0 AlCl\textsubscript{3}:EMIC and Neutral Buffered 1.1:1.0:0.1 AlCl\textsubscript{3}:EMIC:NaCl

For Ni(II) catalyzed ethene dimerizations, 10 mM NiCl\textsubscript{2}[(P(cyclohexyl)\textsubscript{3}]\textsubscript{2} and ca. 0.5 M EtAlCl\textsubscript{3} were added to both a 1.1:1.0 AlCl\textsubscript{3}:EMIC acidic melt and a 1.1:1.0:0.1 AlCl\textsubscript{3}:EMIC:NaCl neutral buffered melt. The two SILMs were prepared and tested as described above. The time-dependent hydrocarbon fractions in the product streams for the acidic and neutral buffered melts are summarized in Fig. 2 and 3, respectively. In the acidic melt, the Ni(II) catalyst led primarily to a single butene fraction (ca. 50-60\% conversion) with only minor C\textsubscript{3}, C\textsubscript{5}, and C\textsubscript{6} fractions (<10\%). On the other hand, for Ni(II) in the buffered neutral melt, butene was formed at 19\% conversion, but ethane and propane were also produced in substantial quantities. The ethane may result from vaporization and hydrolysis of the EtAlCl\textsubscript{3} cocatalyst; however, additional studies are needed before drawing any detailed mechanistic conclusions. Even so, it is significant that Ni(II) catalyzed dimerizations can be performed in the neutral buffered ionic liquids. The loss in catalytic activity for butene production over time, as seen in Fig. 2, is attributed to volatilization or hydrolysis of the alkylaluminum co-catalyst during the test run. No deactivation is seen in Fig. 3 for the neutral buffered system. This activity retention can be attributed to the lower volatility of the alkylaluminum in the neutral buffered melt, where it exits as EtAlCl\textsubscript{4}⁻.

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19. For a given C₈ fraction, the olefinic components generally elute before the alkane components on the HayeSep-Q column employed for analysis.
Fig. 1. Hydrocarbon fractions for oligomerizations in acidic and neutral buffered SILMs.
Fig. 2. Ethylene oligomerization in 1.1:1.0 AlCl₃:EMIC with 10 mM NiCl₂[P(cyclohexyl)₃]₂ + 0.5 M EtAlCl₂. Left axis: C4; Right axis: C3, C5, C6.

Fig. 3. Ethylene oligomerization in 1.1:1.0:0.1 AlCl₃:EMIC:NaCl with 10 mM NiCl₂[P(cyclohexyl)₃]₂ + 0.5 M EtAlCl₂.