Supported Ionic Liquid Membranes (SILMs) were employed to study the catalytic hydrogenation of propene to propane using a 10% Pd/C heterogeneous catalyst. The SILM configuration was asymmetric in nature with the solid Pd/C catalyst confined to the permeate side of the membrane reactor. Using a catalyst loading of approximately 25 µg cm⁻² (based on Pd metal), the heterogeneous catalytic activity was found to follow the order EMI(Imide) > DMPF₆ > BMMF₆ > EMI(Triflate) > EMIBF₄. High catalyst activity was also found for a noncomplexing perfluorinated oil used in place of the ionic liquid. In addition, propene solubility in the ionic liquids was determined to be a function of both the perfluoroanion and the aliphatic nature of the cation and followed the order DMPF₆ > BMMF₆ > EMI(Imide) > EMIBF₄ > EMI(Triflate). Activity and solubility results are consistent with earlier studies on SILMs containing a homogeneous hydrogenation catalyst.
EXPERIMENTAL

The preparations of ionic liquids used in the SILM studies have been described in detail elsewhere.\textsuperscript{2,5} The 10\% by weight Pd on carbon (10\% Pd/C) was obtained from Aldrich and was used as received. Heterogeneous catalytic hydrogenation SILMs were prepared by applying a slurry of the 10\% Pd/C mixed with the desired ionic liquid onto one side of a hydrophobic poly(vinylidene fluoride) Millipore Durapore filter membranes (HVHP 04700, thickness = 125 \mu m, pore size = 0.45 \mu m, porosity = 70\%). The ionic liquid flowed into the pores of the polymer support, leaving the catalyst particles on the outer surface. Also, the ionic liquid wetted the catalyst particles and acted as an adherent coating to keep the catalyst particles attached to the membrane surface. The 10\% Pd/C catalyst loading on the membrane surface was typically ca. 0.25 mg cm\textsuperscript{-2}, corresponding to only 25 \mu g cm\textsuperscript{-2} of Pd metal. All catalyst loadings are reported in terms of \mu g Pd metal per cm\textsuperscript{2} of filter membrane support. The final catalyst membrane was loaded into the membrane reactor setup illustrated in Figure 1 with the catalyst particles on the permeate side of the membrane reactor. In this SILM asymmetric configuration, the palladium is rapidly activated by a H\textsubscript{2} flow over the permeate side of the membrane, and the propene feed gas is hydrogenated after it passes through the bulk of the membrane and reaches the catalyst reaction layer on the permeate side. The membrane and overall reaction scheme are depicted in Figure 2.

The membrane reactor was a Gelman 47-mm inline filter holder fitted with Swagelock\textsuperscript{\textregistered} Quick-Connect couplings. This filter holder uses an O-ring sealing mechanism and has an active membrane area of 12.6 cm\textsuperscript{2}. During catalyst experiments, the feed side of the membrane was held static at 1 atm propene, while the permeate side was constantly swept with a flow (nominally 10 cm\textsuperscript{3} min\textsuperscript{-1}) of H\textsubscript{2} at 1 atm as well. 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 equipped with a TCD detector and controlled with the Peaksimple software program. A silica gel column was used to analyze the permeate gas for propene and propane. All experiments were performed at ambient temperature, ca. 21-22 \degree C.

For each SILM catalyst run, the feed side of the membrane was evacuated and back-filled three times with propene, while the permeate was being swept with a helium purge. The permeate side of the membrane was then switch to a H\textsubscript{2} flow (nominally 10 cm\textsuperscript{3} min\textsuperscript{-1}) and allowed to equilibrate for ca. 10 min before sampling the permeate gas stream. Samples of the permeate were sent to the GC every 15 to 30 min. For reporting purposes, the time for the first sample was taken to be zero.

From the GC data, propene and propane peaks were integrated to determine \% conversion \([100\% \times (\text{propane})/(\text{propane} + \text{propene})]\) as a function of catalyst reaction time, and the average permeability coefficient \((P)\) of the propene was calculated from the total flux of propane and propene measured in the permeate stream. Permeability coefficients were calculated from the standard equation

\[
\text{Flux} = P \cdot A \cdot (\Delta p/\Delta l) \cdot (\text{porosity/tortuosity}) 
\]  

\text{(1)}
where $P$ is the gas permeability coefficient expressed in barrers (1 barrer = 1 cm$^3$(STP)-cm X 10$^{-10}$/cm$^2$-s-cmHg), $A$ is the active membrane area (12.57 cm$^2$), $\Delta p$ is the pressure across the membrane ($\approx$ 76 mm Hg or 1 atm), $\Delta l$ is the membrane thickness (1.25 x 10$^{-2}$ cm), porosity is taken as 0.70, and the tortuosity is taken as 1.

RESULTS AND DISCUSSIONS

Propene Hydrogenation as a Function of Palladium Loading with EMIPF$_6$ SILMs

Supported Ionic Liquid Membranes were prepared with EMIPF$_6$ (EMI = 1-ethyl-3-methylimidazolium) using Pd loading levels of 3, 16, and 58 μg cm$^{-2}$. Figures 3 displays % conversion as a function of run time from $t = 0$ (initial GC sample injection) to 300 min (Fig. 3A) and to 1500 min (Fig. 3B). Because the SILM operates under steady-state feed and permeate conditions, the rate of hydrogenation will remain constant with time as long as the catalyst maintains a constant activity. Clearly, for lower Pd loadings, the Pd/C catalyst decreases in activity over time. With 16 μg cm$^{-2}$, the catalytic activity reaches a conversion of ca. 40% after 300 min and then becomes essentially constant, while a loading of 3 μg cm$^{-2}$ shows continued activity decline until the run was stopped after 316 min. Importantly, with 58 μg cm$^{-2}$, the catalytic activity shows little or no decline in activity even after a total run time of 1441 min.

At this time, we can only speculate on the reasons for declining catalyst activity with low Pd loadings. However, a likely explanation is the presence of impurities in the ionic liquid that slowly “poison” the surface of the Pd catalyst – possible impurities include halide ions, free imidazole base remaining from the initial imidazolium halide preparation, or impurities in the KPF$_6$ used in preparing EMIPF$_6$.

To minimize variability in catalytic activity as a function of run time, Pd loading levels of ca. 25 μg cm$^{-2}$ were employed for subsequent experiments.

Propene Hydrogenation with 10% Pd/C SILMs as a Function of Ionic Liquid

Several heterogeneous Pd/C-catalyzed SILMs were prepared with different ionic liquids and with fluorolube, a perfluorinated oil typically used to prepare infrared samples. Fluorolube was chosen because it has a minimal vapor pressure, is noncomplexing, and is expected to mimic the perfluoroanions of the ionic liquids. Palladium loading was >20 μg cm$^{-2}$ in all cases to minimize loss in catalytic activity. Figure 4 displays % conversion of propene to propane as a function of run time for SILMs prepared with EMI(Imide), EMI(Triflate), EMIBF$_4$, BMIIPF$_6$, DMPBF$_4$, and fluorolube (Imide = (CF$_3$SO$_2$)$_2$N', Triflate = CF$_3$SO$_3$', BMI = 1-butyl-3-methylimidazolium, DMP = 1,2-dimethyl-3-propylimidazolium). For all SILMs, no decline in hydrogenation activity is seen over the course of each experiment.

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DMPIBF₄, the catalytic activity gradually increases before becoming constant, an effect that may be attributed to the slow diffusion of hydrogen to the Pd catalyst sites.

To rank catalytic activity of the various SILMs, the % conversion at 120 min for each run are used for comparison purposes. Table I summarizes the important parameters for these experiments: SILM composition, Pd loading, propene permeability coefficients (P), % conversions at 120 min, and propene solubilities (S). Propene diffusion coefficients (D) are taken from reference 2, and propene solubilities are calculated from the relationship \( P = D \times S \). The second set of propene solubility data shown in the last column are taken from reference 2 for SILMs using homogeneous Rh(I) catalysts.

Based on % conversions at 120 min, the ranking of the ionic liquids for heterogeneous catalysis with Pd/C is EMI(Imide) > DMPIBF₄ > BMIPF₆ > EMI(Triflate) > EMIBF₄. This result can be compared to the ordering EMI(Imide) > EMI(Triflate) > EMI(BF₄) > BMIPF₆ ≈ DMPIBF₄ found for Rh(I) homogeneous catalysis. While caution should be exercised when comparing heterogeneous systems to homogeneous ones, it is interesting to note that catalyst activity is highest with EMI(Imide) in both the heterogeneous and homogeneous systems. In addition, the high gas permeability coefficient \( (i.e., \text{high flux}) \), of the EMI(Imide) SILM translates to the highest overall reactor throughput of all the ionic liquid systems. Finally, it is noteworthy that the fluorolube SILM showed the highest activity of all the systems investigated; although, fluorolube is expected to be a poor solvent for standard homogeneous systems.

The solubilities of propene in the various ionic liquids were calculated in this work and were found to follow the order DMPIBF₄ > BMIPF₆ > EMI(Imide) > EMI(BF₄) > EMI(Triflate). This ordering is similar to that determined previously for the homogeneous catalyst SILMs (last column in Table I), with only EMIBF₄ and EMI(Triflate) swapping positions in the ranking. These results are again consistent with an aliphatic cation and large perfluoroanoion increasing the solubility of olefin in the ionic liquid.

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Table I. Hydrogenation of Propene to Propane with Heterogeneous 10% Pd/C SILMs.

| Ionic Liquid | Pd Loading $\mu$g cm$^{-2}$ | Conversion @ 120 min | $P_{\text{propene}}$ (bars)$^a$ | $D$ (x $10^{-7}$) cm$^2$ s$^{-1}$ | $S_{\text{propene}}$ mol L$^{-1}$ atm$^{-1}$ | $S_{\text{propene}}$ mol L$^{-1}$ atm$^{-1}$ |
|--------------|-----------------------------|----------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| EMIBF$_4$    | 21                          | 37                   | 109                            | 5.0                             | 0.074                           | 0.055$^e$                       |
| EMI(Triflate)| 25                          | 54                   | 57                             | 4.1                             | 0.047                           | 0.098                           |
| DMPIBF$_4$  | 26                          | 62                   | 36                             | 0.2                             | 0.61                            | 0.47                            |
| BMIPF$_6$   | 57                          | 56                   | 62                             | 1.0                             | 0.21                            | 0.17                            |
| EMI(Imide)  | 26                          | 73                   | 239                            | 6.4                             | 0.13                            | 0.14                            |
| Fluorolube  | 31                          | 79                   | 130                            | ---                             | ---                             | ---                             |

$^a$1 barrer = 1 cm$^3$(STP)-cm $\times$ $10^{-10}$/(cm$^2$-s-cmHg). $^b$Electrochemically determined ferrocene diffusion coefficient. $^c$From this work. $^d$From reference 2. $^e$EMIBF$_4$ solubility is an average of two values from reference 2.

Figure 1. Supported Ionic Liquid Membrane (SILM) reactor setup with GC analysis.
Propene (1 atm static)

Reaction Layer ← D_{Propene} ← Ionic Liquid Supported in Porous Polymer Filter Membrane

H₂ (10 cm³ min⁻¹) + 10 wt% Pd on Carbon in Reaction Layer → H₂ + Propane/Propene

To GC for Analysis

Figure 2. Schematic of propene hydrogenation with asymmetric SILM arrangement.

Figure 3. Hydrogenation of propene to propane in SILM showing data to 300 min (A) and to 1500 min (B). Palladium loading levels, µg cm⁻²: 3 (open triangles), 16 (solid triangles), and 58 (solid circles).
Figure 4. Hydrogenation of propene to propane in SILMs made with different ionic liquids and fluorolube. Palladium loadings are given as µg Pd per cm² of membrane. Figure 4A: EMI(Imide), 27 µg cm² (solid circles); EMI(Triflate) 25 µg cm² (open triangles); EMIBF₄, 21 µg cm² (solid triangles). Figure B: Fluorolube, 31 µg cm² (open circles); BMIPF₆, 58 µg cm² (solid inverted triangles); DMPIBF₄, 26 µg cm² (solid inverted triangles).