

Ionic liquid–polymer gel catalytic membrane

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A novel catalytic membrane for heterogeneous hydrogenation is fabricated by incorporating palladium into a gas-permeable ionic liquid–polymer gel composed of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate and poly(vinylidene fluoride)–hexafluoropropylene copolymer.

We have recently described the preparation and properties of novel ionic liquid–polymer gel electrolytes for application in a variety of electrochemical devices.¹ The gels are freestanding, flexible films composed of an air-stable, room-temperature ionic liquid and poly(vinylidene fluoride)–hexafluoropropylene copolymer [PVdF(HFP)]. The ionic liquids consist of a perfluorinated anion (*e.g.* BF₄⁻, CF₃SO₃⁻, PF₆⁻) and a 1,3-dialkylimidazolium cation (*e.g.* 1-ethyl-3-methylimidazolium) and can have either hydrophilic or hydrophobic character.² Although many of the synthetic routes to the ionic liquids require expensive, environmentally undesirable reagents, such as silver salts, we have developed convenient, low-cost routes to high-purity hydrophilic and hydrophobic ionic liquids which make them readily available for research and commercial applications.³

A series of ionic liquids based on the 1-*n*-butyl-3-methylimidazolium cation (BMI⁺) were recently demonstrated to be versatile solvents for homogeneous catalysis.⁴ The catalysis was performed in a two-phase liquid–liquid design which greatly facilitates product recovery while maintaining the catalyst in the reactive ionic liquid phase. Gas-permeable membranes can also function as two-phase catalyst systems and can be engineered to enhance the desired chemical reactions.⁵ The non-volatile ionic liquids have already been demonstrated as effective membrane materials for gas separations when supported within a porous polymer support.⁶ Additionally, while ionic liquids composed of perfluorinated anions have only recently garnered interest as reaction media, other ionic liquids, particularly moisture-sensitive chloroaluminates, are well documented to be effective solvents for organic, inorganic and electrochemical reactions.⁷ The efficacy of chloroaluminates as media for organometallic preparations is illustrated by recent reports of reductive carbonylation⁸ and Friedel–Crafts acylation⁹ of cyclopentadienyl complexes.

To take advantage of the ionic liquids as catalyst solvents and of the ruggedness of the ionic liquid–polymer gels, we have prepared ionic liquid–polymer gels containing a heterogeneous palladium catalyst. These composite materials were tested as a propene hydrogenation catalyst in a membrane configuration.

A typical ionic liquid–polymer catalytic membrane was prepared by mixing 0.044 g 10 mass% Pd on activated carbon (Pd/C, Aldrich), 1.08 g BMIPF₆,^{3,4} and 0.576 g PVdF(HFP) (Kynar Flex 2801-00, Elf Atochem) with 3 ml 4-methylpentan-2-one (MP) under ambient conditions. This mixture was poured into an aluminium weighing pan of 5 cm diameter and was gelled by heating on a hot plate set at *ca.* 75 °C. The MP was allowed to evaporate overnight in ambient air. The final composite membrane was a flexible, dimensionally stable film with thickness *ca.* 0.06 cm and area *ca.* 14 cm², giving a total palladium metal loading of only *ca.* 0.3 mg cm². The ionic liquid imparts ionic conductivity and flexibility to the otherwise insulating, rigid PVdF(HFP) copolymer.

Fig. 1 shows two optical images of the membrane taken at 200× magnification with an inverted metallurgical microscope.

The left-hand image was taken using reflected light and shows a few black Pd/C catalyst particles protruding through the otherwise featureless polymer gel surface. The right-hand image, taken in transmitted light with the focal plan positioned inside the membrane, clearly shows individual Pd/C particles dispersed throughout the membrane interior.

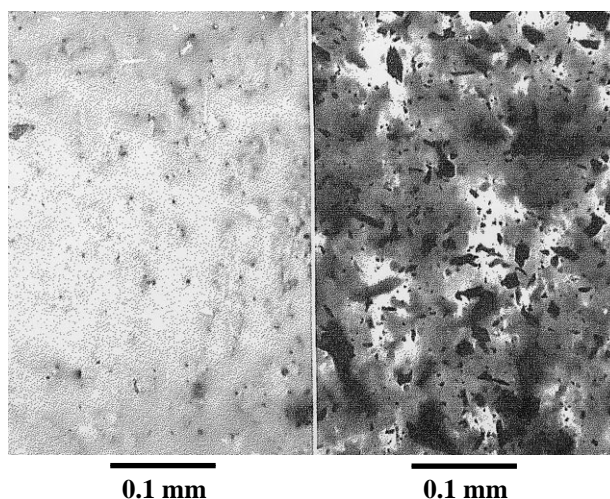


Fig. 1 Optical images at 200× magnification showing the surface (left, reflected light) and interior (right, transmitted light) of the ionic liquid–polymer catalytic membrane

The ionic liquid–polymer membrane was loaded into a catalyst membrane reactor† and evaluated using propene hydrogenation as a model reaction. The propene permeability coefficient (P_{propene}) for the membrane was 300 barrers.‡ Fig. 2 summarizes the data collected for propene hydrogenation as a function of time, where $t_R = 0$ corresponds to the initial introduction of H₂ over the permeate side of the membrane. The flux of propene through the membrane decreased as the flux of propane increased, while the total flux (flux propene + flux

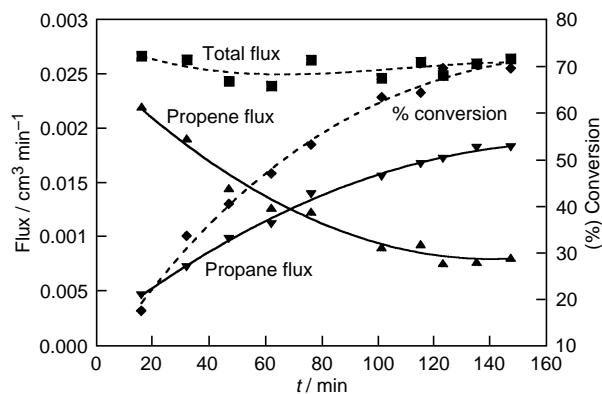


Fig. 2 Plots of propene flux (▲), propane flux (▼), total flux (■) and % conversion (◆) as a function of time

propane) remained constant throughout the experiment. The conversion reached 70% after 2 h and remained constant after this time. We attribute the gradual rise in catalytic activity to the fact that the Pd/C particles are uniformly distributed throughout the ionic liquid–polymer gel structure, and so H₂ on the permeate side of the membrane must diffuse through the membrane interior to the catalyst sites. The time dependence of the fluxes for propene and propane follows $t^{1/2}$ behaviour, consistent with a diffusion-controlled model.

Ionic liquid–polymer gel membranes are a versatile matrix for exploring catalytic processes in the presence of a variety of ionic liquids.¹ Also, because the high ion concentration (*ca.* 3 M) is not detrimental to catalytic activity, these gel electrolytes may be useful for electrocatalytic applications.

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Footnotes

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† The membrane reactor was a Gelman 47 mm inline filter holder fitted with Swagelok Quick-Connect couplings for connection to feed and permeate gases. The filter holder used an O-ring sealing mechanism which gave an effective membrane area of 9.6 cm². During membrane experiments, the feed side of the membrane was contacted with static propene gas at 1 atm, while the permeate side was swept with H₂ at 10.5 cm³ s⁻¹ STP. The permeate gases were vented through a manual sample loop which was used to inject 1 ml samples into a gas chromatograph for analysis with a silica gel column and a TCD detector.

‡ 1 barrer = 10⁻¹⁰ × 1 cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹.

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