Development of “Green” Process for Preparation of High Performance Elastomers: from ab Initio Synthesis to Catalytic Latex Hydrogenation, then to Catalyst Recovery

Hui Wang, Lijuan Yang, Qinmin Pan, and Garry L. Rempel*
Department of Chemical Engineering, University of Waterloo (Canada)
*grempe@cape.uwaterloo.ca

Introduction
The central challenge that is inherent to almost all latex hydrogenation systems and preventing the commercialization of latex hydrogenation of diene-based polymers, pertains to the optimal interplay of accelerating the hydrogenation rate, decreasing the demanded quantity of catalyst, and eliminating the use of organic solvents [1a]. Presented here are our recent efforts to meet this dilemma through decreasing the dimensions of the polymer substrate for the latex hydrogenation process and developing an advanced catalyst recovery process from the catalyst retained latex rubbers.

Materials and Methods
The substrate for catalytic hydrogenation was poly(acrylonitrile-co-butadiene) (NBR) nanoparticles which were prepared in-house via a semibatch emulsion polymerization using GS 12-3-12 (CMC~0.63 g/L) as the emulsifier. The particle size was shown in Table 1. The detailed preparation procedures and characterization of the NBR nanoparticles has been reported previously [1b]. A typical protocol of latex hydrogenation of diene-based polymers including NBR can be found in ref [1a]. A new separation process of extracting catalyst from the HNBR latex nanoparticles was developed by using CO2-expanded liquids (CXLS) with the presence of CO2 in the polymer phase was found to greatly improve the extraction process by preventing the commercialization of latex hydrogenation of diene-based polymers, pertains to the optimal interplay of accelerating the hydrogenation rate, decreasing the demanded quantity of catalyst, and eliminating the use of organic solvents [1a]. Presented here are our recent efforts to meet this dilemma through decreasing the dimensions of the polymer substrate for the latex hydrogenation process and developing an advanced catalyst recovery process from the catalyst retained latex rubbers.

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Results and Discussion
NBR was targeted as the model polymer because it plays a significant role in today’s industry, especially the automotive industry. We synthesized a series of NBR nanoparticles via a semibatch emulsion polymerization system. The diameter can be controlled within the range of 17-54 nm with narrow particle size distributions. The produced nanoparticles exhibit a uniform spherical morphology. The prepared unsaturated nanoparticles were employed as the substrates for the latex hydrogenation in the presence of RhCl(PPh3)3. When 17 nm nanoparticles were used as the substrates, a high conversion of 95 mol% was obtained within 18 h using only 0.1 wt% RhCl(PPh3)3 (Table 1). Very high TOF (~303 h-1) and TON (1102) were achieved for 0.1 wt% catalyst loading. This latex hydrogenation process was completely free of organic solvents and no crosslinking was found. The CXL technology in conjunction with the chelating ligand PMDETA was developed for the recovery of organometallic catalysts, i.e., Wilkinson’s catalyst from polymers, such as HNBR. The presence of CO2 in the polymer phase was found to greatly improve the extraction process by depressing the viscosity of HNBR and increasing its permeability. The mass transfer resistance within HNBR matrix was thereby considerably reduced. After 9 h of operation at 80 °C and 60 bar, only 59 ppm Rh was found to remain in the HNBR particles. The extraction equilibrium was chemically determined. RhCl(PPh3)3 was considered to undergo dissociation of its TPP ligand at elevated temperatures and the CN group of HNBR has a strong coordination with these Wilkinson’s complexes RhCl(PPh3)n(n ≤ 2), which constitutes the central challenge involved in separation of the catalyst from the HNBR-catalyst matrix. The extraction process and the challenges involved are illustrated in Figure 1 [2].

Table 1. Selected Principal Kinetic Data of the Hydrogenation Reaction of NBR

| Diameter (nm) | RhCl(PPh₃)₃ (wt%) | T (°C) | Time reach 95 mol% conv. (h) | k’ (h⁻¹) | E_a (kJ/mol) | TON | TOF (h⁻¹)
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<td>~30</td>
<td>0.13</td>
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<td>130</td>
<td>~20</td>
<td>0.6</td>
<td>--</td>
<td>11066</td>
<td>~553</td>
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*The rate constant k’ and apparent activation energy E_a are determined based on the apparent first-order reaction in [C=C]; TON is defined as the moles of double bonds hydrogenated per mole of rhodium; TOF is defined as the moles of double bonds hydrogenated per moles of rhodium per hour.

Figure 1. Reactions involved in the extraction process for separation of RhCl(PPh₃)₃ from HNBR by the means of CO2-expanded methanol and PMDETA (© 2012 Elsevier).

Significance
We have developed a complete “green” process for preparation of high performance elastomers, which consists of an ab initio polymer synthesis, catalytic reaction, and catalyst recovery. This study may contribute to the improvements of present commercial processes for producing desired elastomers.

References