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Hydrogenation of acrylonitrile-butadiene rubber latex using in situ synthesized $RhCl(PPh_3)_3$ catalyst

Yin Liu, Zhenli Wei, Qinmin Pan**, Garry L. Rempel*

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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ABSTRACT

Catalytic hydrogenation of acrylonitrile-butadiene rubber (NBR) latex was achieved by using in situ synthesized $RhCl(PPh_3)_3$ catalyst. Water-soluble rhodium salt ($RhCl_3$) was used as the catalyst precursor which was reacted in situ with triphenylphosphine (PPh_3) to form $RhCl(PPh_3)_3$. Compared with using solid $RhCl(PPh_3)_3$, hydrogenation of NBR latex using the in situ $RhCl(PPh_3)_3$ showed a faster hydrogenation reaction. Based on the retention of catalyst in the polymer, it was revealed that the efficiency of in situ synthesis and the diffusion of the catalyst from the aqueous phase into the polymer particles were crucial in achieving the required high degree of hydrogenation. As a result, it was discovered that by introducing a small amount of alcohol (e.g. $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, ethanol/total NBR latex = 1/10 volume ratio) to the feed latex, the in situ synthesized catalyst could be used in the hydrogenation reaction very efficiently.

1. Introduction

Diene-based polymers such as butadiene rubber (BR), chloroprene rubber (CR), natural rubber (NR), acrylonitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) are some of the most important commercial polymers [1]. They are widely used as various rubber components in the automobile, petrochemical, mining and aerospace industries. A common feature of these diene-based polymers is the presence of the olefinic structures in the polymer chain which are very active sites for a variety of chemical reactions (e.g. hydrogenation, hydroformylation, metathesis, coupling reactions). The chemical modification of diene based polymers via hydrogenating the unsaturated C=C bonds (C=Cs) has been extensively investigated in academia and industry over the last two decades which has obtained significant achievements [2–4]. Hydrogenation of NBR is an excellent example and it has been commercialized by Bayer (now known as LANXESS) and ZEON Chemicals under the trademark Therban® and Zetpol® respectively. The hydrogenated NBR (HNBR) improves the chemical, physical and mechanical properties of the NBR elastomer. It imparts excellent resistance to oxidative and ozonolytic aging, improved resistance to oils and fluids, even at high temperatures and reduced gas permeability.

Currently, NBR hydrogenation reactions are carried out in polymer solutions using Rh or Pd metal based catalysts. However, the high manufacturing cost of this process has substantially limited its application (i.e. substitution of NBR). The challenge that rubber material scientists and engineers face is to produce this high-performance elastomer in an economical manner. Significant research has been carried out to improve NBR hydrogenation process, including using ruthenium (Ru) or osmium (Os) based catalysts [5,6], biphasic catalysts [7–9], performing hydrogenation reaction in aqueous system [10–17], ionic liquids [18,19], or via the use of supercritical CO_2 [20]. Among them, direct hydrogenation of the NBR in latex becomes especially attractive and considerable efforts have been made to realize direct NBR latex hydrogenation. NBR latex hydrogenation is much more complicated than that in solution especially when it comes to finding an effective catalyst. NBR latex hydrogenation using organometallic catalysts has been investigated a lot. However, the stability of the catalyst in an aqueous system and the necessity of adding a large amount of organic co-solvent (improve the solubility of catalyst in water) as well as the catalyst recovery presents major obstacles in NBR latex hydrogenation.

Our group has been deeply involved in the development of polymer modification processes over the last two decades, and we have focused our efforts on developing effective catalytic processes (i.e. new catalysts, novel reaction processes) for polymer hydrogenation. Recently, we reported that NBR latex could be successfully hydrogenated using $RhCl(PPh_3)_3$ catalyst with the addition of triphenylphosphine (PPh_3) [21] and high quality HNBR latex was obtained. However, the low solubility of the $RhCl(PPh_3)_3$ catalyst

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* Corresponding author. Tel.: +1 519 888 4567x32702.
** Corresponding author. Tel.: +1 519 888 4567x37111.
E-mail addresses: qpan@uwaterloo.ca (Q. Pan), grempel@uwaterloo.ca (G.L. Rempel).

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in an aqueous system negatively affected the efficiency of the catalyst.

As we know, $RhCl_3$, the most common rhodium salt, has high solubility in water. It was preferably adopted as a rhodium precursor for the rhodium catalyst synthesis. The in situ synthesized $RhCl(PPh_3)_3$ in NBR latex using $RhCl_3$ and PPh_3 for NBR latex hydrogenation is reported for the first time in this paper.

2. Experimental

2.1. Materials

Ultra-high purity hydrogen (99.999%, oxygen-free) and high purity nitrogen (99.9%) were purchased from Praxair Inc. (Kitchener, Canada). Commercial grades of NBR latex and solid $RhCl(PPh_3)_3$ catalyst were received from LANXESS Deutschland GmbH (Germany). Reagent grade chemicals such as monochlorobenzene (MCB), methanol, ethanol, 2-propanol, methyl ethyl ketone (MEK) and tetrahydrofuran (THF) were obtained from Fisher-Scientific Canada and used as received. Rhodium trichloride hydrate (RhCl3.aq, Rh 38∼40%) and triphenylphosphine (Reagent Plus 99.9 wt.%) were obtained from Sigma–Aldrich (Canada).

2.2. Hydrogenation of NBR Latex using in situ synthesized $RhCl(PPh_3)_3$ catalyst

NBR latex hydrogenation reactions were conducted in a stirred, 300 mL batch reactor (Parr Instrument, USA). The reactor was cleaned by washing thoroughly with MEK and drying in an oven over night before each reaction. The reaction temperature was monitored using a thermocouple. The catalyst precursor $RhCl_3$ was placed in a catalyst addition device (Parr Instrument, USA) installed in the head of the reactor. PPh_3 was pre-added to the NBR latex before assembling the reactor. The mixture was degassed and heated to the reaction temperature under agitation. After that, $RhCl_3$ was charged to the mixture with hydrogen gas. The hydrogen pressure and reaction temperature were kept constant throughout the reaction period. The reaction mixture was sampled during the reaction.

2.3. Determination of the degree of hydrogenation

The degree of hydrogenation was obtained via Fourier-transform infrared (FT-IR) analysis (Bio-Rad FTS 3000MX spectrometer) using ASTM D5670-95 test method. The NBR latex sample was precipitated by slowly dropping a NaCl solution (10 wt.%) into the latex under agitation. After the solvent was decanted, the precipitated rubber was washed with water and dried under reduced pressure. The dried solid rubber was re-dissolved in MEK and the polymer solution was cast onto a single NaCl crystal disc and dried. The degree of hydrogenation was calculated from the FT-IR spectra according to the peak strength [22].

2.4. Determination of rhodium concentration in HNBR

HNBR samples were digested in a High Pressure Asher (Anton Parr, Austria) using the following method: 0.4 g of HNBR sample was accurately weighed out and mixed with hydrochloric acid (1 mL, 37.5 wt.%), nitric acid (5 mL, 62 wt.%) and aqueous hydrogen peroxide (1 mL of 30%, v/v). The sample was then digested at 300 °C, 130 bar (1885 psi) for 3 h. The rhodium concentration was measured by inductively coupled plasma atomic emission spectroscopy (TELEDYNE, LEEMAN Labs, Prodigy, high dispersion ICP, USA) [23]. The calibration standards were prepared using rhodium trichloride solution (1000 ppm, Sigma–Aldrich) and yttrium (Y) was used as internal reference standard.

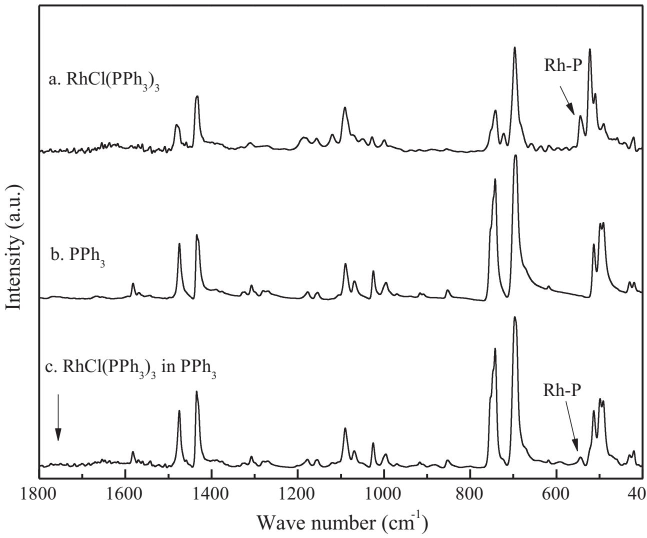

Fig. 1. FT-IR spectra of different solid materials (a) $RhCl(PPh_3)_3$, (b) PPh_3, (c) precipitates [$RhCl(PPh_3)_3$ in PPh_3] from in situ synthesis in water. Reaction condition for (c): 100 mL H_2O, $T = 145\,^{\circ}C$, $t = 15$ min, $RhCl_3 = 0.052$ mmol, 1.8 mmol PPh_3.

2.5. Particle size in latex and its distribution

The size and number size distribution (non-negative least squares method) of the polymer particles of the synthesized latex were determined at 25 °C using a Nanotrac 150 particle size analyzer (BETATEK Inc. Toronto, Canada) and reported as the number average diameter. The calculations of the particle size distributions were performed using Microtrac FLEX 10.2.14 software available from BETATEK Inc., which employed single-exponential fitting, non-negatively constrained least-squares (NNLS), cumulants analysis, and CONTIN particle size distribution analysis routines.

3. Results and discussion

3.1. In situ synthesis of $RhCl(PPh_3)_3$ and its activity in NBR latex hydrogenation

We first investigated the in situ synthesis of $RhCl(PPh_3)_3$ in pure water. It was found that solid PPh_3 liquefied around 80 °C. After adding $RhCl_3$, the color of PPh_3 droplets quickly changed from transparent to red. This could be explained by the formation of $RhCl(PPh_3)_3$ from $RhCl_3$ and PPh_3. The formed $RhCl(PPh_3)_3$ has a burgundy color. Due to its hydrophobicity, $RhCl(PPh_3)_3$ tends to stay in the PPh_3 droplet. As a result, the color of the droplet changes from colorless to red. When the system cooled down to room temperature, these red droplets solidified and precipitated.

Fig. 1 shows the FT-IR spectrum of $RhCl(PPh_3)_3$ (a), pure PPh_3 (b) and the precipitate obtained after $RhCl_3$ reacted with PPh_3 (c), respectively. From the FT-IR results, although the spectrum of the precipitate is similar to that of PPh_3, the distinctive peak at 550 cm^{-1} attributed to a Rh-P stretching vibration was observed, confirming the formation of $RhCl(PPh_3)_3$ [24]. After carefully washing with hot ethanol to remove the PPh_3, most of the precipitates (PPh_3) were re-dissolved. The final residue analyzed by FT-IR spectroscopy showed the same spectrum as that of $RhCl(PPh_3)_3$. In addition, the yield was calculated based on the feed $RhCl_3$. It was found that less than 20 mol.% of rhodium from the feed $RhCl_3$ could be converted to $RhCl(PPh_3)_3$ in water.

Representative experiments under operational conditions and final conversions of NBR latex hydrogenation using the in situ synthesized $RhCl(PPh_3)_3$ catalyst as well as the pre-made solid $RhCl(PPh_3)_3$ catalyst are listed in Table 1. Two reaction