

Catalytic Hydrogenation of Nitrile–Butadiene Copolymer Emulsion

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ABSTRACT: Two processes have been developed for the selective hydrogenation of the C=C bonds in nitrile–butadiene rubber emulsions (NBR emulsions) in the presence of a number of $\text{RuCl}_2(\text{PPh}_3)_3$ complex catalysts. One of the processes is carried out in a homogeneous system, in which an organic solvent, which can dissolve the NBR polymer and catalyst and which is compatible with the emulsion, is used. The other process is carried out in a heterogeneous system, in which an organic solvent which is capable of dissolving the catalyst and swelling the polymer particle but is not miscible with the aqueous emulsion phase, is used. In both processes, quantitative hydrogenation of the C=C bonds of the NBR emulsion is achieved in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$. It is also found that the addition of certain types of additives can improve the activities of the Ru-based catalysts. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 667–675, 1997

Key words: polymer hydrogenation; nitrile rubber hydrogenation

INTRODUCTION

Excellent durability of a rubber engineering component has become an increasingly important requirement as elastomers are used for more critical engineering applications and applied in more aggressive environments.^{1,2} The durability issue of rubber components is further complicated by a change in the expectation for the life of the elastomer in the automobile industry. It is expected that in the near future rubber components should be able to last the lifetime of the vehicles. Thus the improvement of the performances of existing rubber materials against aging under aggressive environments has become a very important issue.

Acrylonitrile–butadiene rubber (NBR) has been widely used in the automobile and oil industries to make parts such as belts and seals. For improved performance, it requires higher heat and oxygen resistance, good resistance to swelling by aggressive fluids, good mechanical properties, and outstanding wear resistance under extremely adverse conditions. The nitrile groups in NBR provide the polymer high oil resistance; however, the presence of unsaturated C=C bonds in this elastomer might undergo degradation or oxidation in a hot and/or oxidizing environment. Therefore, in the past 20 years, extensive research and development work has been conducted on selective hydrogenation of the butadiene content of NBR. In 1975 one of the approaches investigated at Bayer led to the development of a new class of elastomers with superior oil, fuel, chemical, abrasion, and ozone resistance—hydrogenated nitrile rubber (HNBR),^{3,4} which is now available under the tradename Therban. The saturated nature and the nitrile groups present in the macromolecular structure impart the property combination out-

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lined above. In 1984, Rempel and Azizian patented a process for hydrogenating NBR in the presence of $\text{RhH}(\text{PPh}_3)_4$.⁵ Pd carboxylate salts have also been used as catalysts for the selective hydrogenation of NBR by Nippon Zeon Co. Ltd.⁶⁻⁸ Although hydrogenation of NBR has become a very important process for the production of oil-resistant elastomers with superior thermal and oxidative stability,⁹⁻¹² the price of these HNBR materials is still very high, which has substantially limited the application of HNBR materials. The challenge facing rubber material scientists and engineers is to produce high-performance elastomers that do not unduly raise their prices. Efforts have been made to use Ru complexes as catalysts for the hydrogenation of NBR, since Ru metal is much cheaper than Rh and Pd metals.¹³⁻¹⁶ Quantitative hydrogenation of NBR by $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, $\text{RuCl}(\text{CO})(\text{OCOR})(\text{PPh}_3)_2$, and some other Ru complexes has been reported under relatively mild reaction conditions.^{17,18} Another way to invent more efficient and cheaper processes for the production of HNBR is to use NBR emulsion obtained from the emulsion polymerization process directly for hydrogenation.¹⁹⁻²¹ By applying such a process, the usual procedures for the NBR hydrogenation, such as the precipitation of NBR polymer from its emulsion, the drying process, and the redissolution of the polymer into an organic solvent, can be avoided. This would certainly represent an economic advantage for industrial production of HNBR. Another advantage of such processes is the formulation of polymer emulsions which do not contain $\text{C}=\text{C}$ bonds in the polymer chain. This type of emulsion may have potentially important applications for the coating industry.²²⁻²⁴ In the following, two processes for the direct hydrogenation of NBR emulsion have been investigated and the results are presented.

EXPERIMENTAL

Apparatus

The hydrogenation reactions were carried out in a 300 mL glass-lined Parr autoclave equipped with a thermocouple which is connected with a temperature monitoring system, a catalyst addition device, a sampling port/outlet, and a high-speed propeller stirring device. The autoclave is also equipped with a gas inlet and outlet in order

to introduce and release the H_2 . A Parr temperature and agitation controller were used for monitoring temperature and stirring rate, respectively. A Parr autoclave heating mantel was used for heating the autoclave.

Materials

Reaction Gases

The reaction gas used in the hydrogenation was oxygen-free zero gas hydrogen obtained from Linde.

Solvents

Reagent grade methyl ethyl ketone (MEK) was obtained from Caledon Laboratories Ltd. Ethanol, acetone, tetrahydrofuran, dimethylsulfoxide (DMSO), dimethylformamide (DMF), and 3-pentanone were purchased from Aldrich. All solvents were used as received.

Catalysts

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ was obtained from Engelhard Industries and was used as received. All the other catalysts used for this study were prepared according to literature procedures.²⁵⁻²⁹

NBR Emulsion

The NBR emulsions used for this study were NBR emulsion (A) with 18 wt % of polymer solid, both obtained from Polysar Rubber Corp. (now Bayer Inc.). The terminal vinyl $\text{C}=\text{C}$ bonds in the butadiene content are $\sim 4-5\%$.

Hydrogenation Process

All the reactions were carried out in a stainless steel autoclave. The NBR copolymer emulsion was mixed with the organic solvent(s) in a 250 mL glass liner. The catalyst was weighed and placed into a catalyst addition device. The glass liner was then put into the autoclave and the autoclave was assembled. The mixture in the autoclave was degassed by bubbling hydrogen gas through for 5-10 min at 0.2 MPa hydrogen pressure. The autoclave was then pressurized to 1.2 MPa with hydrogen and the reaction system was heated to the desired reaction temperature with agitation. When the temperature of the autoclave was stabilized, the catalyst addition device was pressurized to the reaction pressure with hydrogen in order

Table I NBR Emulsion Hydrogenation (Process I): Investigation of Different Catalysts

Catalyst	Reaction Conditions	Results
RhCl(PPh ₃) ₃	Rh/NBR: 0.23 wt %; 20 h; 160°C ^a	No hydrogenation
RhH((PPh ₃) ₄	Rh/NBR: 0.094 wt %; 4 h; 100°C ^b	Most of the vinyl C=C in NBR polymer has been hydrogenated
RuCl(CO)(OCOPh)(PPh ₃) ₂	Ru/NBR: 0.25 wt %; 20 h; 160°C ^a	Very little hydrogenation
RuHCl(CO)(PPh ₃) ₄	Ru/NBR: 0.094 wt %; 5 h; 150°C ^b	No hydrogenation
RuCl ₂ (PPh ₃) ₂	Ru/NBR: 0.094 wt %; 1–2 h; 150°C ^b	>95% hydrogenation
RuCl(CO)(Styryl)(PCy ₃) ₂	Ru/NBR: 0.094 wt %; 2 h; 150°C ^b	No hydrogenation

RuCl(CO)(Styryl)(PCy₃)₂: carbonylchlorostyrylbis(tricyclohexylphosphine) ruthenium (II); RuCl₂(PPh₃)₃: dichlorotris(triphenylphosphine) ruthenium (II); RuCl(CO)(OCOPh)(PPh₃)₂: chlorobenzoato(carbonyl)bis(triphenylphosphine) ruthenium (II); RuHCl(CO)(PPh₃)₄: Carbonylchlorohydridotris(triphenylphosphine) ruthenium (II). H₂ pressure for all the reactions: 8.3 MPa.

^a NBR Emulsion: 12.5 mL; MEK: 115 mL.

^b NBR Emulsion: 22 mL; MEK: 80 mL.

to drop the catalyst into the solution. Samples were taken for IR or NMR analysis during the reaction. Hydrogen gas was pressurized into the autoclave when required in order to maintain a constant reaction pressure throughout the reaction period.

Characterization

Infrared Spectroscopic Analysis

The infrared spectra of NBR and hydrogenated NBR polymers were obtained with a Nicolet 520 FTIR. The infrared samples were prepared by casting polymer films on sodium chloride disks in an oven maintained at 100°C.

Nuclear Magnetic Resonance Spectroscopic Analysis

¹H-NMR results were used to calculate the degree of hydrogenation for different reaction systems. All the samples were analyzed on a Bruker 250 MHz instrument. Deuterated chloroform was used as the solvent in all cases.

RESULTS AND DISCUSSION

Two processes have been developed for the direct hydrogenation of NBR emulsion. Process I is a homogeneous catalytic hydrogenation system. The key factor for this hydrogenation process is to find a solvent which is miscible with the emulsion phase and which can also dissolve the polymer and catalyst. Solvents such as MEK, acetone, and tetrahydrofuran (THF) are potentially good solvents for such a process. Process II involves a heterogeneous catalytic hydrogenation system. In this system, an organic solvent which is not miscible with the emulsion phase is used. In this system, the organic solvent can only swell the polymer particles in the emulsion. The suitable solvent should also be capable of dissolving the catalyst. Solvents such as chlorobenzene and toluene are good solvents. Furthermore, a small amount of a second solvent can be added to this reaction system in order to accelerate the hydrogenation rate. This second solvent must be miscible with the emulsion phase as well as the organic solvent; therefore it can speed any interaction be-

Table II NBR Emulsion Hydrogenation in the Presence of Added Ferrous Ammonium Sulfate (Process I)

Catalyst	Ru/NBR (wt %)	Additive (g)/0.01 g Ru	Reaction Time (h)	Hydrogenation (%)
RuCl ₂ (PPh ₃) ₃	0.0958	0.72	4	96
RuCl(OCOPh)(CO)(PPh ₃) ₃	0.108	0.64	10	91
RuCl(CO)(Styryl)(PCy ₃) ₂	0.1054	0.66	0.8	99
RuHCl(CO)(PPh ₃) ₃	0.0923	0.75	2.8	90

Table III NBR Emulsion Hydrogenation in the Presence of Added Carboxylic Acid

Carboxylic Acid	Ru/NBR (wt %)	Additive/0.01 g Ru	Reaction Time (h)	Hydrogenation (%)
None	0.0056		2	0
Chloroacetic acid	0.0056	0.82	<3	99
Citric acid	0.0056	1.38	<4	99
3-Chloro-propionic acid	0.0056	0.94	<2.3	99
Succinic acid	0.0056	0.82	2.7	99
1,4-Phthalic acid	0.0056	0.82	3.7	98

Process I Catalyst: RuCl(CO)(Styryl)(PCy₃)₂. Twenty-two milliliters emulsion B and 100 mL MEK were used for each reaction run. H₂ pressure: 6.9 MPa.

tween those two phases. MEK and acetone are good choices for such a purpose.

A summary of the results of the investigation on these two processes is now presented.

Hydrogenation of NBR Emulsion (40 : 65) by Process I

The key part of process I is to have a solvent which can destroy the surface interaction of the polymer particles in the emulsion and dissolve the polymer into the resulting solvent-emulsion mixture. This will create a homogeneous polymer-solvent system. Using a catalyst which is soluble in this mixture will result in a homogeneous hydrogenation system. The following provides a summary of investigations using different catalysts, solvents, and reaction conditions for this process.

A number of known hydrogenation catalysts were investigated for NBR emulsion hydrogenation using process I. The results are summarized in Table I.

All these catalysts investigated are active catalysts for a conventional NBR hydrogenation process (i.e., NBR solid was dissolved into an organic solvent before subjecting to hydrogenation). However, the only efficient hydrogenation catalyst for quantitative NBR hydrogenation of emulsion, in the presence of an organic solvent, appeared to be RuCl₂(PPh₃)₃. It seems that the presence of the emulsion system has significantly reduced the activity of the other Ru and Rh catalysts under investigation. It is suspected that some of the additives and the large amount of water in the NBR emulsion could have poisonous effects on some of the hydrogenation catalysts.

Table IV Effects of Different Solvents on NBR Emulsion Hydrogenation by Process I

Solvent	Results
MEK ^a	>95% Hydrogenation
THF	>95% Hydrogenation
Acetone	>95% Hydrogenation
Dimethylsulfoxide	NBR emulsion was not soluble in the resulting mixture, no hydrogenation
Dimethylformamide	NBR emulsion was not soluble in the resulting mixture, no hydrogenation
3-Pentanone	NBR emulsion was not soluble in the resulting mixture, no hydrogenation, some crosslinking occurred

Reaction conditions: solvent, 115 mL; emulsion A, 12.5 mL; catalyst, RuCl₂(PPh₃)₃; Ru/NBR, 0.093 wt %; temperature, 150°C; H₂ pressure, 8.3 MPa.

^a MEK, methyl ethyl ketone.

Table V Effect of Polymer Concentration on Degree of Hydrogenation via Process I

NBR Emulsion Amount (mL)	Results
25 mL (4.5 g NBR)	~ 85–89% hydrogenation in 3 h, 90% hydrogenation after 10 h
12.5 mL (2.25 g NBR)	~ 95% hydrogenation in 1 h

Reaction conditions: solvent, 115 mL; catalyst, $\text{RuCl}_2(\text{PPh}_3)_3$; Ru/NBR, 0.093 wt %; temperature, 150°C; H_2 pressure, 8.3 MPa.

Efforts had been made to neutralize the poison effect of the emulsion system by using certain additives during the hydrogenation process. Two classes of additives were found to be very effective: one includes inorganic additives such as ammonium sulfate, ferrous sulfate, ferrous ammonium sulfate, etc.; the other class includes carboxylic acids.^{30,31} Although the reaction mechanisms of these additives during the hydrogenation of NBR emulsion are not clearly understood, the effectiveness of these additives in improving the activities of Ru-based catalysts was very significant. Table II gives the NBR emulsion hydrogenation results of different catalysts in the presence of ferrous ammonium sulfate. In addition to $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RuCl}(\text{OCOPh})(\text{CO})(\text{PPh}_3)_3$ and $\text{RuCl}(\text{CO})(\text{Styryl})(\text{PCy}_3)_2$ are also active catalysts toward the NBR emulsion hydrogenation by process I with the addition of a small amount of ferrous ammonium sulfate. Among these catalysts, $\text{RuCl}(\text{CO})(\text{Styryl})(\text{PCy}_3)_2$ appeared to be the most active catalyst.

Table III shows the results of NBR emulsion hydrogenation in the presence of a small amount

Table VI Effect of Reaction Temperature on NBR Emulsion Hydrogenation via Process I

Reaction Temperature (°C)	Results
150	~ 95% hydrogenation in 1 h; ~ 98% hydrogenation in 2 h
120	~ 95% hydrogenation in 0.7 h, ~ >100 hydrogenation in 2 h
100	In ~ 50 min, there is still vinyl content left in the polymer

Reaction conditions: solvent, 115 mL; emulsion A, 12.5 mL (2.25 g NBR); catalyst, $\text{RuCl}_2(\text{PPh}_3)_3$; Ru/NBR, 0.093 wt %; temperature, 150°C; H_2 pressure, 8.3 MPa.

of added carboxylic acid. A number of carboxylic acids were found to be very effective in preventing the poisoning of catalyst $\text{RuCl}(\text{CO})(\text{Styryl})(\text{PCy}_3)_2$ by the emulsion system.

Different solvents were used for the NBR emulsion hydrogenation catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$ via process I. Table IV shows the results of this study. This investigation shows that only those solvents which can destroy the surface interaction of the polymer particles in the emulsion, and thus bring the emulsion into the solvent, are good solvents for process I. MEK, THF, and acetone are good examples of this type of solvent.

The hydrogenation of NBR emulsion catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$ under different reaction conditions was investigated. The results are given in Tables V–VIII.

Table V shows the effect of polymer concentrations on the degree of hydrogenation. It is believed that the presence of water (from the emulsion) in the reaction mixture reduced the solubility of the hydrogenated NBR. Therefore, at high polymer concentration, the partially hydrogenated polymer precipitated out from the solution, which resulted in a lower degree of hydrogenation.

Table VI shows the effect of reaction temperature on the degree of hydrogenation. It seems that 120–150°C is the best temperature range for this hydrogenation system. At 100°C, the activity of the $\text{RuCl}_2(\text{PPh}_3)_3$ catalyst is rather low.

Table VII shows the results obtained from reactions using different Ru concentrations. It seems that ~ 0.09 wt % (Ru/polymer) is the suitable amount of $\text{RuCl}_2(\text{PPh}_3)_3$ catalyst to be used in a reaction in the temperature range of 120–150°C. At lower reaction temperature (i.e., 100°C), a higher catalyst loading is needed to obtain a reasonable reaction speed to be used in a reaction in the temperature range of 120–150°C. At lower reaction temperature (i.e., 100°C), a higher cata-

Table VII Effect of RuCl₂(PPh₃)₃ Concentration (Process I)

Ru/Polymer (wt %)	Other Conditions	Hydrogenation (%)
0.187%	12.5 mL emulsion, catalyst added as solid; 1. 150°C; 2. 100°C	1. after 0.5 h, 95%; after 1.1 h, 98% 2. after 1 h, 88%; after 3 h, 98%
0.093%	12.5 mL emulsion, catalyst added as solid; 1. 150°C; 2. 100°C	1. <1 h, 95%; <2 h, 98% 2. after 0.8 h, there is still vinyl content
0.047%	6.7 mL emulsion, catalyst added as solid	After 0.5 h, some vinyl C=C hydrogenation No further reaction afterward
0.047%	12.5 mL emulsion, catalyst added as solvent	After 0.5 h, only the vinyl content is reacted

Reaction conditions: solvent, 115 mL; H₂ pressure, 8.3 MPa; catalyst, RuCl₂(PPh₃)₃. Emulsion A was used.

lyst loading is needed to obtain a reasonable reaction speed.

Table VIII provides the summary of the results for the effect of hydrogen pressure on the rate of NBR emulsion hydrogenation. It seems that in the hydrogen pressure range of 6.9 Mpa to 8.3 Mpa, the hydrogenation can achieve 95% within a few hours of reaction time. At a lower hydrogen pressure, the reaction becomes quite slow.

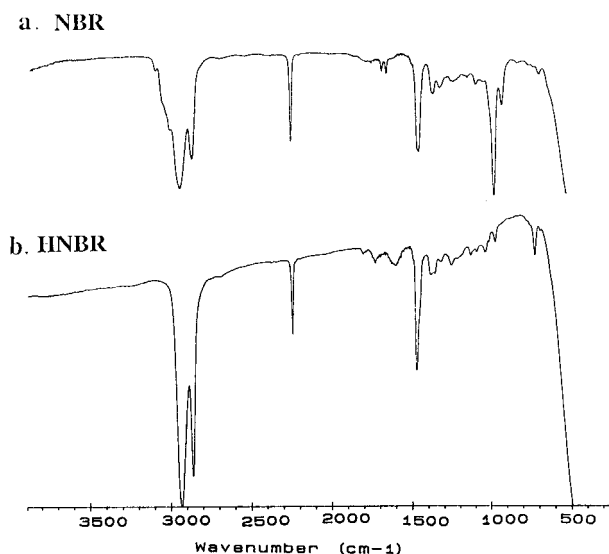
The structure of the HNBR polymer was characterized by ¹H-NMR and FTIR. IR spectra for the hydrogenated polymer and for the starting NBR material are shown in Figure 1(a,b). For the starting NBR material in Figure 1(a), the peak at 2250 cm⁻¹ is attributed to the CN groups in the NBR polymer. The very weak band at 3085 cm⁻¹ is assigned to the C—H stretching band for the =CH₂ (vinyl) group of the starting NBR polymer. The relatively small peak at 920 cm⁻¹ is attributed to the CH₂ wagging of the 4–5% vinyl group. The strong neighbor peak centered at 980

cm⁻¹, which is assigned to the CH wagging of the trans alkene structure in the NBR polymer. Spectrum b in Figure 1 is the IR spectrum for the >95% hydrogenated NBR. The disappearance of all characteristic absorbances of C=C suggests nearly quantitative hydrogenation of the C=C bonds. The retaining of the same intensity of the characteristic absorbance for CN groups at 2250 cm⁻¹ indicates that the hydrogenation is highly selective toward C=C bonds. Figure 2(a,b) show the ¹H-NMR spectra for NBR and HNBR obtained from process I. In spectrum 2a, the peaks centered at 5.5 ppm are attributed to the olefinic protons (—CH₂—CH=CH—CH₂—) in the 1,4-PBD structure; the very small peaks near 5.15 ppm are assigned to the olefinic protons (—CH=CH₂) of

Table VIII Effect of Hydrogen Pressure (Process I)

Hydrogen Pressure (MPa)	Results
8.3	~ 95% hydrogenation in 1 h; ~ 98% hydrogenation in 2 h
6.9	~ 93% hydrogenation in 1 h
5.5	~ 80% hydrogenation in 1 h
4.1	~ 80% hydrogenation in 1 h; ~ 83% hydrogenation in 4.5 h

Reaction conditions: solvent, 115 mL; emulsion A, 12.5 mL (2.25 g NBR); catalyst, RuCl₂(PPh₃)₃; Ru/NBR, 0.093 wt %; temperature, 150°C.

**Figure 1** IR spectra for (a) NBR; (b) HNBR.

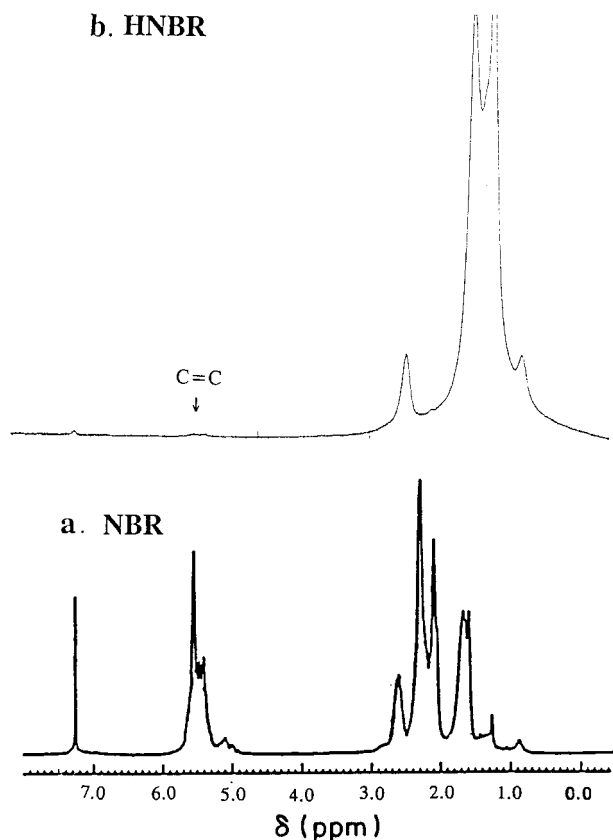


Figure 2 $^1\text{H-NMR}$ spectra for (a) NBR; (b) HNBR.

the 4–5% vinyl group content present in the NBR polymer. Figure 2(b) is the $^1\text{H-NMR}$ spectrum for HNBR, the peaks in the olefin proton region have almost completely disappeared from this spectrum. Integration of this spectrum showed >98% hydrogenation.

Although the catalyst was not recovered in this study, techniques have previously been developed

to recover precious metals upon completion of the hydrogenation reaction.³²

Hydrogenation of NBR Emulsion (40 : 65) by Process II

Process II is a heterogeneous reaction system in which an organic solvent is used to swell the polymer particles of the emulsion. The possible advantage of this process is that the polymer emulsion can be retained during and after the hydrogenation reaction. However, due to the heterogeneous nature of the reaction, it is expected that this system will not be as active as process I.

Three different Ru complexes were investigated as catalysts for process II: dichlorotris(triphenylphosphine) ruthenium (II); chlorobenzotriphenylphosphine ruthenium (II); and carbonylchlorohydridotris(triphenylphosphine) ruthenium (II).

In this investigation, the organic solvent used for this study was monochlorobenzene (MCB), a second solvent, MEK, was used to accelerate the reaction. The results of this investigation are given in Table IX. It is found that only $\text{RuCl}_2(\text{PPh}_3)_3$ is capable of hydrogenating >95% of the C=C bonds of the NBR polymer in its emulsion form via process II. It is believed that this second solvent can behave as a phase transfer mediator and thus accelerate the interaction between the organic solvent phase and the emulsion phase. Experimental results (see Table IX) show that the NBR emulsion hydrogenation rate is much slower for the reaction without the second solvent (91% hydrogenation in 11 h).

The effects of reaction temperature, catalyst concentration, polymer loading, and hydrogen

Table IX Hydrogenation of NBR Emulsion via Process II

Catalyst	Reaction Conditions	Results
$\text{RuCl}_2(\text{PPh}_3)_3$	Ru/polymer: 0.183 wt %; 11 h (90 mL MCB)	91% hydrogenation
$\text{RuCl}_2(\text{PPh}_3)_3$	Ru/polymer: 0.183 wt %; MEK: 10 mL; 4.5 h	95% hydrogenation
$\text{ClRuH}(\text{CO})(\text{PPh}_3)_3$	Ru/polymer: 0.2 wt %; MEK: 10 mL; 17 h	Hydrogenation of the vinyl C=C content only
$\text{ClRu}(\text{CO})(\text{OCOPh})(\text{PPh}_3)_2$	Ru/polymer: 0.1 wt %; MEK: 10 mL; 17 h	Hydrogenation of the vinyl C=C content only

H_2 pressure, 8.3 MPa; NBR emulsion A, 23 mL; MCB (monochlorobenzene), 80 mL; temperature, 150°C; MEK, methyl ethyl ketone.

Table X NBR Emulsion Hydrogenation Under Different Conditions via Process II

Reaction Conditions	Results
Ru/NBR: 0.09 wt %; NBR/solvent: 4 wt %; temperature: 150°C; H ₂ pressure: 8.3 MPa	70% hydrogenation in ~ 1 h, 95% hydrogenation in ~ 4.5 h
Ru/NBR: 0.045 wt %; NBR/solvent: 4 wt %; temperature: 150°C; H ₂ pressure: 8.3 MPa	<60% hydrogenation in ~ 1 h, 80% hydrogenation in ~ 2 h; no more reaction
Ru/NBR: 0.09 wt %; NBR/solvent: 2 wt %; temperature: 150°C; H ₂ pressure: 8.3 MPa	70% hydrogenation in 0.7 h, 93% hydrogenation in 2.5 h, >95% hydrogenation in 3.5 h
Ru/NBR: 0.09 wt %; NBR/solvent: 2 wt %; temperature: 130°C; H ₂ pressure: 8.3 MPa	80% hydrogenation in 4 h, 90% hydrogenation in 6 h, >95% hydrogenation in 11 h
Ru/NBR: 0.09 wt %; NBR/solvent: 2 wt %; temperature: 150°C; H ₂ pressure: 6.9 MPa	85% hydrogenation in 1.5 h, 90% hydrogenation in 4 h, 92% hydrogenation in 11 h

Reaction conditions: MCB, 80 mL; MEK, 10 mL; catalyst, RuCl₂(PPh₃)₃. Emulsion A is used.

pressure were also investigated for process II. The results are listed in Table X. The effect of catalyst concentration can be seen from the comparison of the hydrogenation results for experiment 1 and 2. When the polymer loading is 4 wt %, the degree of hydrogenation decreases from 95% to 80% due to the reducing of Ru loading from 0.09% to 0.047%. The hydrogenation results from experiment 1 and 3 show that the hydrogenation rate is slightly increased by reducing the polymer loading from 4 to 2 wt %; however, both runs proceeded at a reasonable rate. The effects of temperature and H₂ pressure are also listed in Table X. It seems that reaction temperature and H₂ pressure have a significant effect on the hydrogenation rate. The results from runs 3 and 4 show that the reaction time needed to reach 95% hydrogenation increases from 3.5 to 11 h when the reaction temperature decreased from 150 to 130°C. When the H₂ pressure for the reaction is 8.3 MPa, the degree of hydrogenation reaches 95% in ~ 3.5 h; when it is only 6.9 MPa, the degree of hydrogenation only reaches 92% over a much longer reaction period (11 h).

CONCLUSIONS

NBR emulsion obtained from commercial polymerization processes was used directly under hydrogenation conditions in the presence of different known hydrogenation catalysts via two processes. One of the processes was carried out in a homogeneous system, the other was a heterogeneous reaction system. RuCl₂(PPh₃)₃ was found to be an active catalyst for both processes. It was found that the addition of a small amount of additives

such as ferrous ammonium sulfate and certain carboxylic acids could neutralize the poisonous effect of the emulsion system on some Ru-based catalysts.

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