Catalytic Hydrogenation of Nitrile Rubber Using Palladium and Ruthenium Complexes

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ABSTRACT: The catalytic hydrogenation of acrylonitrile-butadiene copolymer (nitrile rubber, NBR) using $Pd(OAc)_2$ or $RuCl_2(PPh_3)_3$ catalysts has been investigated in order to produce a totally saturated nitrile rubber. The hydrogenation of NBR is effective with both catalysts and achieved total conversion under the appropriate reaction conditions. In the case of palladium the effects of reaction parameters such as reaction temperature, pressure, time, catalyst concentration, and NBR concentration have been investigated. Even though both ruthenium- and palladium-based catalysts are effective in the production of HNBR, the former requires harsh reaction conditions and has the drawback of gel formation under high conversion, motivating the migration to $RuCl_2(PPh_3)_3$ as an alternative catalyst. The degree of hydrogenation was determined by IR and NMR spectroscopy. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 659–663, 2007

Key words: hydrogenation; nitrile rubber; catalysis; palladium acetate catalyst; dichloro*tris*(triphenyl)phosphine ruthenium catalyst; characterization of rubber

INTRODUCTION

The hydrogenation of dienes has been the subject of great interest as a method for the modification of elastomers.[1,2] It enables access to products with enhanced chemical properties. A remarkable example of this effect is the reduction of the susceptibility of unsaturated polymers to air and moisture oxidation.[3,4]

Hydrogenated nitrile rubber (HNBR) is more resistant than its unmodified elastomer counterpart to oil and solvents at high temperature, to oxygen and ozone, ultraviolet radiation, abrasion, and chemical attacks.[5,6] Therefore, HNBR has achieved important applications in the petroleum extraction, atomic energy, military, aerospace, and automotive industries.[7,8]

NBR is hydrogenated with molecular hydrogen in the presence of heterogeneous or homogeneous catalysts. The choice of the hydrogenation method and the catalyst system are limited by the presence of cyano groups in the polymer. Hence, the chemoselective hydrogenation of the vinylic double bonds of the nitrile rubber without reduction of the CN group, which would give rise to gel[4,5,9,10] formation due to crosslinking, remains an unresolved problem.

Several rhodium, ruthenium, and palladium complexes[5] have been described as efficient catalysts for such hydrogenation reactions, although their general high cost limits their industrial use. In this work, we have sought to obtain a high performing system capable of hydrogenating NBR with reduction of maximum number of C=C bonds with high selectivity and conversion using less-expensive ruthenium[2,5,9,11,12] and palladium[1,13,14] complexes.

The hydrogenation of NBR in the presence of Pd and Ru containing-complexes has been studied with the main objective to optimize the system in view of the preparation of totally hydrogenated NBR.

EXPERIMENTAL

The hydrogenation reactions were performed with Petroflex NBR 3350 nitrile rubber, containing 32 mol % acrylonitrile, 8 mol % vinylic C=C bonds, and 60 mol % 1,4 C=C bonds.

The reaction solvents, acetone, and methylethylketone, P.A., were supplied by Nuclear Chemicals Industries (Brazil). Palladium acetate and dichloro*tris*(triphenyl)phosphine ruthenium were obtained from Umicore, Brazil. The hydrogen gas used in the hydrogenation experiments was of 99.99% purity.

Hydrogenation runs

The experiments were performed in a 1-L autoclave reactor (Parr Instruments Company, Moline, IL). A typical catalytic run was performed by dissolving
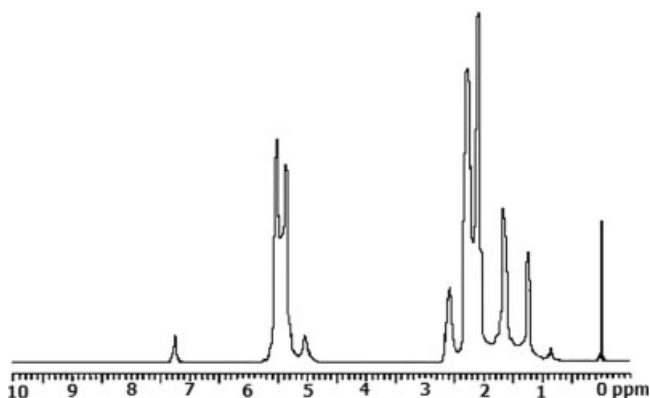
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Figure 1 ^{1}HNMR spectrum of NBR (Petroflex NBR 3350).

2 g NBR sample in 100 mL of acetone. A weighed amount of $Pd(OAc)_2$ (260 μmol) or $RuCl_2(PPh_3)_3$ (31 μmol) was added to the solution. The mixture was introduced into the reactor, which was closed, purged with hydrogen, and the pressure increased to the desired value (40 atm). The autoclave was heated to the desired temperature (140°C), which was maintained over the reaction time (8 h), under vigorous mechanical stirring. After the desired reaction time the polymer was coagulated by pouring the reaction mixture into 5% HCl solution in water and finally dried *in vacuum* until constant weight.

Temperature, pressure, time, catalyst concentration, and NBR concentration were varied to study their effect on the level of carbon–carbon double bond hydrogenation attained.

The activity of the system was measured as the turnover frequency (TOF) which is the number of moles of C=C bonds reduced per mole of transition metal per hour.[15]

Characterization

HNBR was characterized by ^{1}H NMR spectrum recorded[16] on a Varian VXR 200 spectrometer, operated at 200 MHz. The chemical shifts were measured as ppm in $CDCl_3$ relative to TMS as internal standard. A typical ^{1}H NMR spectrum of a NBR sample containing 32 mol % acrylonitrile is shown in Figure 1.

The ^{1}H NMR of hydrogenated NBR obtained with palladium[1] or ruthenium[2,8] catalysts is shown in Figure 2.

The % conversion of C=C bonds to C—C bonds has been calculated by taking the ratio of integral intensities of olefinic proton signals around 5.0–6.0 to that of aliphatic protons in the region 0.7–2.4 ppm.

The hydrogenation of NBR also was followed by IR spectra[16] measured on a Bomem B-102 spectrometer, operating in the spectral width of 4000–650
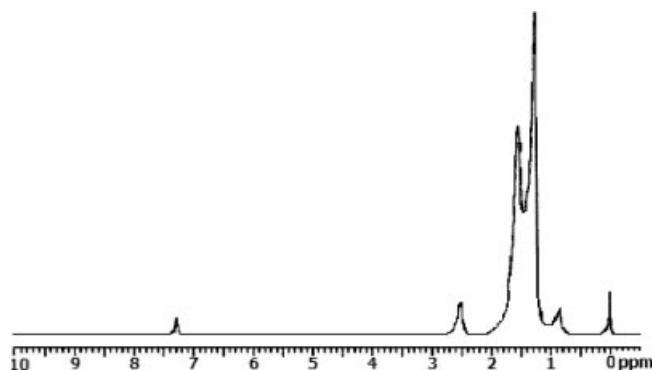
Figure 2 ^{1}HNMR spectrum of HNBR obtained in Run 20; Table II (2 g of NBR, 78 mL of MEK, and 31 μmol of $RuCl_2(PPh_3)_3$).

cm^{-1}. A typical IR spectrum of hydrogenated NBR obtained with palladium and ruthenium catalysts is shown in Figure 3.

RESULTS AND DISCUSSION

Palladium and Ruthenium complexes are effective catalyst for hydrogenation of C=C bonds in NBR. The hydrogenation is affected by various reaction parameters such as temperature, catalyst amount, substrate amount, etc. The effects of these parameters generated from the present study are furnished in Table I, taking $Pd(OAc)_2$ as typical catalyst.

The *reaction temperature* affects the performance of $Pd(OAc)_2$ in the hydrogenation of NBR, as shown in entries at 80–100°C (Runs 4 and 5). At low reaction temperatures (from 25 to 60°C), under 27 atm of hydrogen, the system gives rise to total conversion of the unsaturated moieties. However, with further
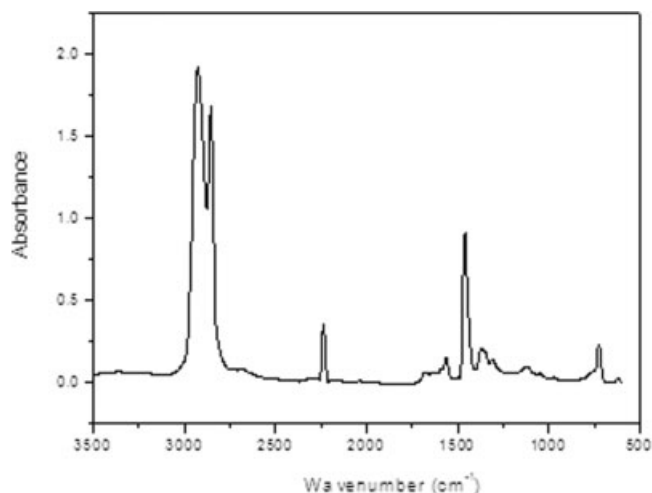

Figure 3 IR spectrum of HNBR obtained in Run 27; Table III (10 g of NBR dissolved in 78 mL of MEK, and 62 μmol of $RuCl_2(PPh_3)_3$).

TABLE I
Hydrogenation of NBR with Pd(OAc)$_2$: Effects of Temperature, Pressure, Amount of Catalyst, Time, and Amount of NBR[a]

Reaction run	Temperature (°C)	Pressure (atm)	Catalyst (μmol)	Time (h)	NBR (g)	Conversion (%) 1,4-*trans*	Total	TOF (h^{-1})
1	**25**	27	260	1	2	100	100	88.5
2	**40**	27	260	1	2	100	100	88.5
3	**60**	27	260	1	2	100	100	88.5
4	**80**	27	260	1	2	84	85	75.4
5	**100**	27	260	1	2	83	82	73.1
6	60	**10**	260	1	2	95	96	84.6
7	60	**20**	260	1	2	96	96	85.4
3	60	**27**	260	1	2	100	100	88.5
8	60	**34**	260	1	2	98	98	86.5
9	60	**40**	260	1	2	92	93	82.3
10	60	27	**53**	1	2	64	69	30.0
11	60	27	**130**	1	2	88	90	159
3	60	27	**260**	1	2	100	100	88.5
12	60	27	**410**	1	2	97	97	55.9
13	60	27	**530**	1	2	60	63	5.7
14	60	27	260	**0.5**	2	83	85	150.3
3	60	27	260	**1**	2	100	100	88.5
15	60	27	260	**1.5**	2	97	97	57.2
16	60	27	260	**2**	2	96	96	42.3
3	60	27	260	1	**2**	100	100	88.5
17	60	27	260	1	**4**	68	73	53.8
18	60	27	260	1	**6**	49	53	84.6
19	60	27	260	1	**10**	35	38	146.1

[a] Conditions: 2 g of NBR, 60°C, 27 atm, 1 h, 100 mL of solvent, and 260 μmol of palladium catalyst.

increase in the reaction temperature the degree of hydrogenation decreases, probably due to deactivation of the catalyst, and selectivity falls and both olefinic and cyano groups are reduced (Runs 4 and 5). Further increase of temperature to 150°C inactivated the catalyst.[5]

Hydrogen pressure has no significant effect on the catalytic performance of palladium acetate (see Runs 6–9 in Table I). The data in Table I imply that under the chosen reaction conditions high double bond conversion has been realized. However, a small drop in conversion was seen at hydrogen pressures >27 atm. This deactivation at high hydrogen pressure has been observed previously for Pd complexes and has been ascribed to aggregation of metal particles formed under such conditions.[5]

The *catalyst concentration* affects the degree of hydrogenation as seen in Runs 12 and 13 (410–530 μmol of Pd(OAc)$_2$). Increasing the amount of catalyst increases the level of hydrogenation, although an excess of the former causes an aggregation phenomenon, diminishing the conversion. The presence of agglomerates deactivates the catalytic system ascribed to the formation of multispecies.

The *reaction time* affects the hydrogenation of NBR, as seen in Runs 15 and 16 (1.5–2 h). The maximum conversion was attained after 1 h of reaction. After this time the conversion is complete and the accuracy of the values are within + or −3%. Longer reaction

times were not necessary to achieve high conversion as evidenced by a decrease in TOF with reaction time.

The system containing a palladium catalyst is effective for the hydrogenation of 2 g of NBR dissolved in 100 mL of acetone under the following conditions: 27 atm of H$_2$, 60°C, 1 h, and 260 μmol of
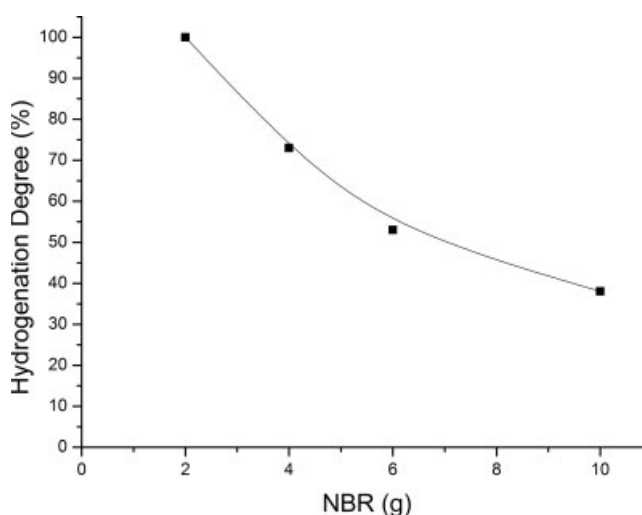

Figure 4 Evolution of the conversion of the 1,4-*trans* carbon–carbon double bonds of NBR (32 mol % acrylonitrile) with 260 μmol of palladium catalyst in 100 mL of solvent versus solid content of NBR.

TABLE II
Hydrogenation of NBR with RuCl$_2$(PPh$_3$)$_3$: Effect of NBR Concentration[a]

Reaction run	NBR (g)	Conversion (%)		Turnover frequency (h^{-1})
		1,4-*trans*	Total	
20	2	100	100	69.3
21	4	66	70	97.6
22	6	51	57	135.5
23	10	47	52	142.2

[a] Conditions: 40 atm, 140°C, 4 h, 78 mL of solvent, and 31 μmol of ruthenium catalyst.

TABLE III
Hydrogenation of NBR with RuCl$_2$(PPh$_3$)$_3$: Effect of Time[a]

Reaction run	Time (h)	Conversion (%)		Turnover frequency (h^{-1})
		1,4-*trans*	Total	
24	2	6	10	40.0
25	4	27	30	57.8
26	6	36	57	56.9
27	8	100	100	97.1

[a] Conditions: 10 g of NBR, 40 atm, 140°C, 78 mL of solvent, and 62 μmol of ruthenium catalyst.

catalyst, as shown in Table I (Run 3). However, increasing the amount of NBR using the same conditions leads to a fall in the degree of hydrogenation. Figure 4 shows this effect.

Studies with RuCl$_2$(PPh$_3$)$_3$ catalyst were performed due to the limited performance of Pd(OAc)$_2$.

Similar experiments were performed with RuCl$_2$(PPh$_3$)$_3$, which has already been shown to be effective in these hydrogenations.[2] The maximum conversion of NBR was 100%, obtained when 2 g of NBR was dissolved in 78 mL of MEK under the conditions: 40 atm of H$_2$, 140°C, 4 h, and 31 μmol of catalyst (Run 20). Table II shows the hydrogenation results for the ruthenium system.

Under these conditions the degree of hydrogenation decreases with the increase of solid content (Runs 20–23). Figure 5 shows this decrement.

By increasing the amount of substrate NBR dissolved in 78 mL of MEK to 10 g, at 40 atm of H$_2$, 140°C, and 62 μmol of catalyst, a maximum conversion, of 100% after 8 h, was obtained (Run 27).
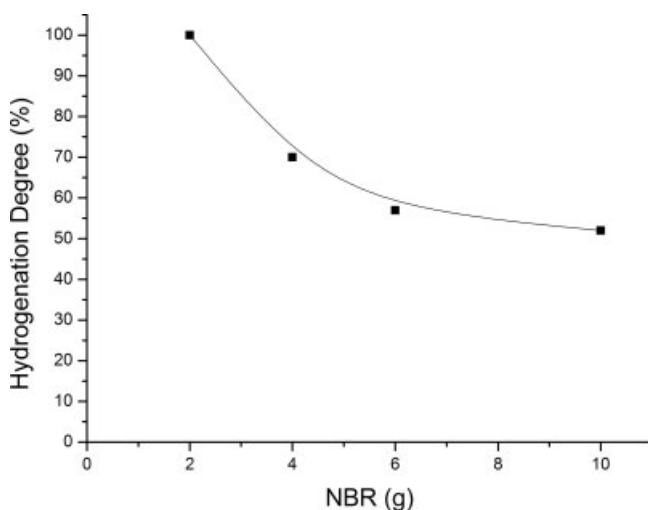
A study of conversion versus time is shown in Table III.

Figure 6 shows the evolution of the hydrogenation in the study alongside time in order to obtain the reduction of the maximum number of C=C bonds in the system with 10 mol % of NBR.

Systems employing the dichloro*tris*(triphenylphosphine) ruthenium(II) complex give products without impregnated metal in the HNBR, although palladium acetate based systems produce darkened polymers, as a consequence of the reduction of Pd(II) to Pd(0).

Comparison of ^{1}H NMR and IR spectra of the obtained products after hydrogenation with those of substrate (NBR) revealed an enhanced intensity of the aliphatic protons at the expense of the olefinic ones. For the unreduced product (^{1}H NMR spectrum in Fig. 1), the peak at 4.9–5.3 ppm can be attributed to the terminal (=CH$_2$), 1,2-vinylic units and the peak at 5.3–5.7 ppm can be attributed to the (—CH=CH—), 1,4(*cis* and *trans*) units. The peak between 2.5 and 2.8 corresponds to acrylonitrile

Figure 5 Evolution of the conversion of the 1,4-*trans* carbon–carbon double bonds of NBR (32 mol % acrylonitrile) with 31 μmol of ruthenium catalyst in 78 mL of solvent versus solid content of NBR.
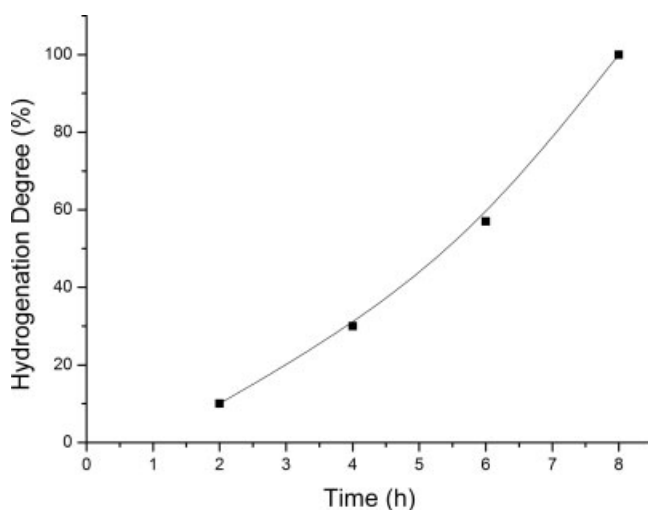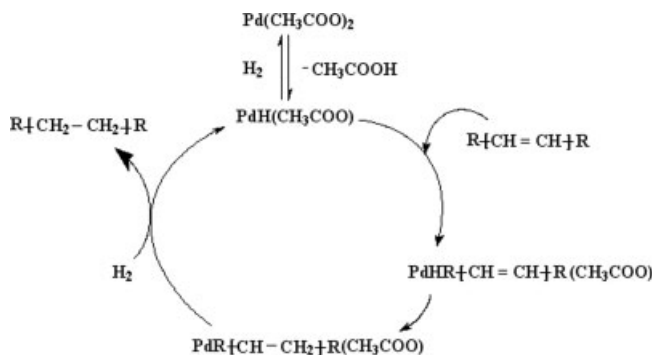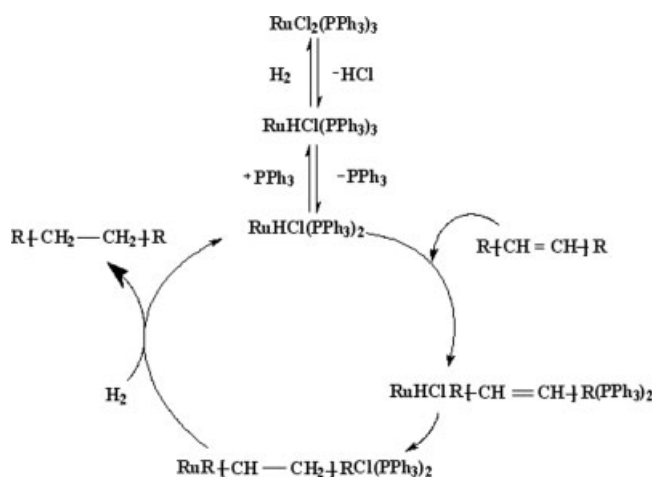

Figure 6 Evolution of the conversion of the 1,4-*trans* carbon–carbon double bonds of NBR (32 mol % acrylonitrile) with 62 μmol of ruthenium catalyst and 10 g of NBR in 78 mL of solvent versus time.

Scheme 1 Plausible mechanism for the Pd(OAc)$_2$ catalyst in the hydrogenation of NBR.

units (—CH—C≡N). Alternatively the conversion can be calculated from the IR spectra shown in Figure 3, where the main IR peaks for the NBR polymer are assigned as: 2235 cm^{-1} (—C≡N stretching); 969 cm^{-1} (=C—H bending – *trans* units); 916 cm^{-1} (=C—H bending – vinylic units). The last two peaks disappear after hydrogenation. HNBR shows improved resistance to oxidative degradation generating one elastomer with improved chemical properties.[5,7,8,17]

The mechanism for the nitrile hydrogenation in the rubber proceeds via metal hydride formation using Pd(OAc)$_2$ or RuCl$_2$(PPh$_3$)$_3$ as catalysts. Primarily, there is an activation of the catalytic species, which reacts with hydrogen to form metal hydride complexes. Subsequently, there are successive coor-

dinations of olefinic bonds of the NBR to the metal center and hydride transfer to the carbon–carbon double bond to give the saturated product. Schemes 1 and 2 show a plausible mechanism for Pd(OAc)$_2$ and RuCl$_2$(PPh$_3$)$_3$ catalysts, respectively.[5,18,19]

In conclusion, it can be stated that systems based on palladium acetate are more active under milder reaction conditions than the analogous ruthenium complexes for hydrogenation processes for 2 g of NBR and 30–60 mg of catalyst, which gave 100% conversion in the former case. For systems with ruthenium complexes the milder conditions led to a lower degree of metal impregnation in the polymer compared with the palladium catalyst.

Using RuCl$_2$(PPh$_3$)$_3$ as a catalyst a maximum reduction of C=C bonds will be achievable without reduction of the cyano group, using ketones as solvents.

Scheme 2 Plausible mechanism for the RuCl$_2$(PPh$_3$)$_3$ catalyst in the hydrogenation of NBR.

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