Effect of Supercritical CO_2 on Bulk Hydrogenation of Nitrile Butadiene Rubber Catalyzed by $RhCl(PPh_3)_3$

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Summary: The effect of supercritical (SC) CO_2 on the bulk hydrogenation of NBR entrapped with the catalyst ($RhCl(PPh_3)_3$) was investigated under various reaction times, reaction temperatures, hydrogen pressures and loadings of the catalyst and the thicknesses of the polymer films. CO_2 helps in improving the transport behaviour of catalyst in polymer matrices, as well as helping to move catalyst into or out of the polymer. A method for the measurement of the dissolution extent or the apparent solubility of the Rh based catalyst in SC-CO_2 was developed. It is found that high temperatures and high SC-CO_2 densities would enhance the apparent solubility. Cosolvents, such as acetone, are also found to increase the apparent solubility. Details on the hydrogenation process are also presented.

Keywords: catalysts; rubber

Introduction

The catalytic hydrogenation of acrylonitrile-butadiene rubber (NBR) is an important post-polymerization process resulting in a more stable and tougher derivative, hydrogenated NBR (HNBR), which is widely used in the automotive industry. However, Due to the use of a large amount of organic solvent and expensive catalysts in the present commercial processes, cost and environmental concerns arise. In recent years we have been pursuing to green the NBR hydrogenation process taking advantage of supercritical fluid (SCF) technology. As a continuation of the previous work[1] which focused on the possibility and feasibility of NBR hydrogenation catalyzed by an osmium-complex in SC-CO_2, we now report on the bulk hydrogenation of NBR using Wilkinson's catalyst ($RhCl(PPh_3)_3$). Some effects of reaction conditions were studied. In addition, the apparent solubility of $RhCl(PPh_3)_3$ in SC-CO_2 was explored by a method developed in this investigation as it is an important factor for the design and understanding of hydrogenation reactions using Wilkinson's catalyst in SC-CO_2.

DOI: 10.1002/masy.200351412

Experimental Apparatus and Method

Apparatus

A 300 ml, 316 stainless steel bench top laboratory batch autoclave reactor (Parr Pressure Reactor, 1L) was used for the solventless gas phase hydrogenation experiments. Figure 1 shows a schematic diagram of the autoclave reactor. The impeller (1) was magnetically driven by the drive housing (7) that was turned by an electric motor controlled by a variac. Stainless steel plates (2) cast with NBR were attached to the impeller bound by stainless steel wire. The reactor temperature was controlled with a PID controller. A type J thermocouple (3) was used to monitor the temperature. The manifold was equipped with a pressure gauge (5) that could not be isolated from the reactor side. A rupture disk (8) was installed as a safety measure to avoid reaction pressure above the pressure limitation of the vessel. The sample tube (4) was not used to take any samples in the present investigation. A glass liner was used in all of the hydrogenation experiments to avoid any possibility of experiencing a catalytic effect of the reactor wall. Hydrogen gas was fed into the vessel through valve 9. A purge exhaust line was provided through valve 6.

In addition, a volume-changeable SFT Phase Monitor Reactor was used for the operations when the operation pressure was beyond 2000psi. The detail was reported in the previous paper.[1]

Material

Ultra high purity hydrogen (oxygen-free) and anaerobic CO_2 (Linde-Union Carbide) were used as received. Catalyst $RhCl(PPh_3)_3$ was prepared according to the literature.[2] The nitrile-butadiene rubber was provided by Bayer Inc. (Krynac 38.50) which contained 62 wt% butadiene (80% trans, 15% cis, and 5% vinyl C=C) and possessed an Mn=70000 and a polydispersity of 3.6.

Preparation of Polymer Samples

NBR samples were prepared by weighing a known amount of polymer (e.g., 5g), catalyst and co-catalyst if required into a vial. A magnetic stirring bar was added to the vial. The vial was sealed and degassed before it was moved into a Vacuum Atmospheres® Glove Box. A certain amount of solvent was charged into the vial using a pipette. The vial was sealed and placed on a magnetic stirrer and the solution was stirred for 12 hours to make sure the solution was homogeneous. The polymer sample was then supported on a mesh or plate.

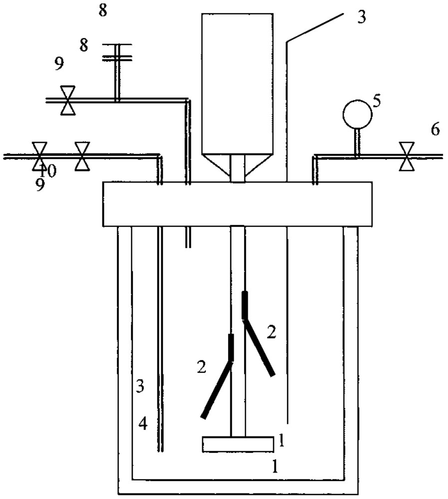

Fig. 1. Catalytic Hydrogenation Autoclave Reactor System: 1. impeller, 2. sample plates, 3. thermocouple, 4. sample tube, 5. a pressure gauge, 6. and 9. valves, 7. the drive housing, 8. a rupture disk.

Measurement Procedures for the Apparent Solubility of Catalyst in SC-CO_2

An NBR sample entrapped with 10 % (wt) $RhCl(PPh_3)_3$ was prepared. The weight of complex entrapped within NBR can be calculated since the ratio of the complex weight to NBR weight was known when the polymer solution was prepared. After degassing the reactor, a certain amount of liquid CO_2 was charged into the reactor. The temperature and pressure in the reactor were recorded in order to calculate the weight of CO_2 charged. The reactor was heated to the required temperature. After the treatment time (30 hours), the system was depressurized and the sample was removed and weighed. The difference in weight was considered to be the amount of complex dissolved in SC-CO_2.

Experimental Results and Discussion

Hydrogenation of NBR without CO_2

Table 1 indicates a typical relationship between conversion and reaction time. The hydrogenation conversion increased quickly during the initial reaction phase. Then about 1 hour later, the reaction conversions slowly increased with the increment of the reaction time. The effect of the hydrogen pressure was shown in Table 2. Higher conversions were obtained at higher hydrogen pressures. However, under the present conditions, the influence of the hydrogen pressure was not so significant. When the pressures increased from 200psig to 1500psig, the hydrogenation conversions were raised from 85.6% to 92.0%.

Table 1. Dependence of the conversions on the reaction times.

Run	t, hr	θ,cm^2/mg-NBR	C,%
1704-5	1.0	0.0941	78.0
1804-4	2.0	0.0864	82.5
1904-1	3.0	0.0788	85.6

Catalyst 0.046 wt %; TPP/Rh=19.5 (wt/wt); Temperature: 140°C; P_{H2}: 2000psig.

Table 2. Effect of pressures on the hydrogenation conversions.

RUN	P_{H2},PSIG	θ,CM^2/MG-NBR	C,%
1904-1	200	0.0787	85.6
0105-3	500	0.0877	84.3
0405-1	800	0.0518	90.3
0805-4	1200	0.0777	90.8
0905-3	1500	0.0984	92.0

Catalyst 0.046 wt %; PPh_3/Rh=19.5 (wt/wt); temperature: 140°C; time: 3.0 hrs.

Table 3. Effect of the thickness on the reaction conversions.

Run	θ,cm^2/mg-NBR	C,%
0905-3	0.0984	92.0
0905-7	0.112	88.5
0905-5	0.127	90.6
0905-6	0.173	86.9

Catalyst 0.046 wt %; PPh_3/Rh=19.5 (wt/wt); temp.: 140°C; P_{H2}=1500; time: 3.0 hrs.

The effect of the thickness θ of the polymer samples was also studied. Table 3 lists the reaction conditions and the results. For the current range of the thickness of polymer samples, the thickness of polymer samples showed little effect on the hydrogenation conversion. The reason is that the catalyst had been entrapped already in the polymer samples and the hydrogen diffusion is not a significant factor, which can be confirmed by a comparison between the hydrogen diffusion resistance and the reaction resistance.

Hydrogenation of NBR in the Presence of CO_2

A weak negative effect was observed by adding CO_2 (see Table 4). This is not overall surprising since there is an offset of two factors: the enhancement of transport property in polymer matrices by CO_2 and the removal of the catalyst from the polymer by CO_2. This effect is further demonstrated in Table 5. The first two runs in Table 5 are the blank experiments without any catalyst. Comparing Run 2703a and Run2303, a similar phenomenon to that mentioned above, that the addition of SC-CO_2 decreased the hydrogenation conversion is observed.

Table 4. Effect of CO_2 on the reaction conversions.

Run	P_{CO2}	P_{H2}	t,hrs	θ,cm^2/mg-NBR	C,%
1704-5	0	200	1.0	0.0941	78.0
2504-6	350	200	1.0	0.0624	66.7
2704-2	650	200	1.0	0.0520	66.7
2404-7	1000	200	1.0	0.0627	65.2
0105-3	0	500	3.0	0.0877	84.3
0205-4	1000	500	3.0	0.0822	82.9
0405-1	0	800	3.0	0.0518	90.3
0505-2	1000	800	3.0	0.0637	88.5

Catalyst 0.046 wt %; PPh_3/Rh=19.5 (wt/wt); T=140°C.

Table 5. Hydrogenation in the SFT Phase monitor reactor.

Run	P_{H2},psig	P_{CO2},psig	θ,cm^2/mg-NBR	Rh/NBR,wt/wt	C, %
1303	1580	0	1.85	0	0
2803	1580	4420	0.30	0	<5
2703a	1580	0	0.32	0.037	100
2303	1580	4420	0.52	0.037	85.6
2403a	1580	4420	0.52	0.037	86.3
2403b	1580	4420	0.52	0	53.9

Temp.=140°C; PPh_3/Rh=19.5 (wt/wt); time=2.5hrs; density of SC-CO_2: 0.88g/ml.

A more interesting phenomenon was observed when two polymer samples were put into the reaction system; one was entrapped with the catalyst (2403a), and another was without any catalyst (2403b). The two samples were arranged without being in contact with each other.

However, more than 53% hydrogenation conversion was obtained for the sample 2403b. This indicated that SC-CO_2 has a powerful swelling capacity for NBR and can significantly move the catalyst into or out of the NBR substrate. This implies that it is feasible to use SC-CO_2 to enhance solventless hydrogenation of NBR and to help in removing catalyst from NBR after hydrogenation.

Dissolving Capacity of $RhCl(PPh_3)_3$ in SC-CO_2

In the above section, it has been found that the catalyst entrapped in a polymer sample could be move out of the polymer sample by SC-CO_2. This part of catalyst was assumed to be the catalyst dissolved in SC-CO_2. This phenomenon provides a potential method to determine the solubility of a transition metal complex in SC-CO_2. The measurement results are not expected to be the same as the solubility of catalysts in SC-CO_2 obtained from other methods.[3-5] However, they could be used as an indicator to possibly estimate the dissolving capacity of the catalyst in SC-CO_2. To express easily, the measurement result was simply called the apparent solubility of a catalyst in SC-CO_2 in this investigation and noted in $\boldsymbol{S}$. The catalyst entrapped in NBR appears to dissolve in SC-CO_2 and consequently the weight of the polymer sample will decrease. However, this process requires a long time to reach equilibrium. As expected this time depends on the treatment temperature and the pressure of SC-CO_2. To determine the time when the equilibrium was reached, a series of measurements were carried out in SC-CO_2 with a density of 0.88g/mL at 60°C and 5200psig. The dependence of the apparent solubility of the catalyst on the treatment time is illustrated in Figure 2. An "S" shape relationship was obtained. When the treatment time was in the range of 15 to 30 hours, the apparent solubility of the catalyst strongly depend on the time. However, after about 30 hours, the apparent solubility essentially was unchanged with time. This indicated that the system had attained equilibrium. Therefore, the treatment time was selected to be about 30 hours in subsequent measurements. Since the weight variation of a NBR sample was attributed to be the amount of the dissolution of the catalyst in SC-CO_2, a NBR sample without any entrapped catalyst should have no ingredients dissolved in SC-CO_2 to result in the weight loss. The blank measurement of a NBR sample was carried out in SC-CO_2 at 32°C and 1100psig. It was found that the weight variation was less than 0.01mg (RunS006 in Table 6, the weight of the NBR sample was 40mg). According to this measurement result (RunS006), the weight variation derived from the NBR itself can be neglected in the subsequent measurements with an acceptable measurement error.

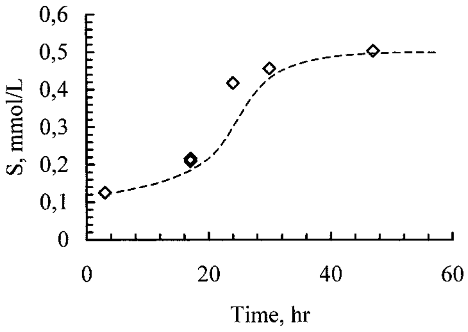

Fig. 2. Dependence of the Apparent Solubility of Wilkinson's Catalyst in SC-CO_2 on the Treatment Time (SC-CO_2 density 0.88g/mL, Temperature 60°C, Pressure 5200psig).

At a specific SC-CO_2 density, the measurement temperatures and pressures will influence the apparent solubilities of the catalyst in SC-CO_2. Run S007, S008 and S011 shown in Table 6 were carried out to compare this influence. Since the density of CO_2 was fixed (0.88g/mL), the increment of the temperatures will increase the system pressures. According to the data in Table 6, high temperatures (or high pressures) will increase the apparent solubilities of the catalyst.

Table 6. Measurement of the apparent solubility of Wilkinson's Catalyst.

Run#	Time, hrs.	T, °C	P_{CO2}, psig	W, mg	ΔW, mg	S, mmol/L
S006	35.5	32	1100	0	~0.01	~0.0
S007*	30	32	4000	4.144	0.590	0.172
S008*	30	60	5700	3.766	1.560	0.456
S009**	30	60	5000	4.055	1.740	0.509
S011*	30	100	8000	3.410	2.110	0.594

W: the weight of the entrapped catalyst; ΔW: the weight variation after the treatment; S: the apparent solubility of the catalyst; * SC-CO_2 density 0.88g/mL; ** 0.5mL acetone was added in this measurement.

Some cosolvents such as acetone can greatly increase the solubility of transition metal complexes in SC-CO_2. On comparison of the results of Run S009 and Run S008 in Table 6, the apparent solubility of the catalyst in Run S009 was higher than that in Run S008 due to the addition of 0.5mL acetone in Run S009.

It should be noted that the amount of the entrapped catalyst within the NBR sample has to be high enough to guarantee the amount of the dissolved catalyst in SC-CO_2 is less than the amount of the entrapped catalyst within a NBR sample. The data in Table 6 indicates that the highest ratio of the weight change to the amount of the entrapped catalyst was less than 50%. In most measurement cases, this ratio was about 10%. Thus the values of solubilities provided are saturation values.

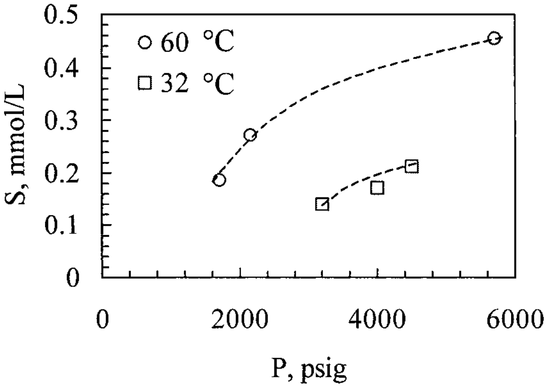

Fig. 3. Apparent solubility of $RhCl(PPh_3)_3$ vs. temperature and pressure in CO_2.

When the measurement temperatures and volumes are fixed, high pressures correspond to high densities of SC-CO_2. Since the density of SC-CO_2 strongly affects the solubility of complexes, it can be expected that the pressures should influence the solubility of complexes significantly. Figure 3 illustrates the pressure effect (or the density effect) on the apparent solubilities ***S*** of the catalyst in SC-CO_2. The SC-CO_2 density corresponding to a specific pressure can be obtained by the measurement of the CO_2 volume charged at room temperature. Since the volume of the CO_2 can not be precisely measured in the present investigation, the SC-CO_2 density derived from this measurement would not be precise. Therefore, only SC-CO_2 pressures were used in Figure 3. At both measurement temperatures (32°C and 60 °C), the apparent solubility of the catalyst increases with the increment of the pressures or densities of SC-CO_2.

Conclusion

The apparent solubility of the catalyst would depend on the measurement temperature and the density of SC-CO_2 according to the above exploratory investigations. High temperatures can raise the apparent solubilities of the catalyst in SC-CO_2 under the same SC-CO_2 density; and the increment of the density of SC-CO_2 also can enhance the apparent solubility of the catalyst in SC-CO_2 when the measurement temperature is the same. The cosolvent such as acetone could greatly enhance the apparent solubility of the catalyst in SC-CO_2.

The measurement of the apparent solubility of transition metal complexes in SC-CO_2 by the method developed in this investigation is just the initial step in this field. Further investigations are required in many respects such as the comparison of data obtained from the present method with the data derived from other quantitative measurement methods. Although we can not compare the measurement conditions with the literature, a value of the solubility of 0.02mM at T=45 °C and P=4010 psig for Wilkinson's catalyst in SC-CO_2 has been reported.[6]

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