Study on Hydroformylation of Octene Catalyzed by Rhodium-Containing Functional Ionic Liquid

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Abstract. Because of the irreplaceable nature of hydroformylation, it has been a hot topic in recent decades. The catalyst for hydroformylation usually takes the transition metal as the center atom. However, the high price of metal restricts the large-scale industrialization of hydroformylation reaction. In this paper, a new type of 1-polyethylene glycol monomethyl ether-3-methyl imidazole rhodium ionic liquid catalyst was used to study the hydroformylation of catalytic octene. The reaction was carried out in a 75mL autoclave. The optimum reaction conditions were obtained by experiments: when the reaction time was 5h, the reaction pressure was 4MPa, and the reaction temperature was 100 ℃, the conversion of octene reached 90.2%, and the yield of nonylaldehyde reached 70.6%. The new ionic liquid catalyst used in the reaction has the characteristics of “high temperature catalysis, low temperature phase separation”. It laid the foundation for the recovery of the catalyst.

1. Introduction
In the late 1930s, German scientist Otto Roelen accidentally discovered the hydroformylation reaction in Ruhchemie’s research work on Fisher-Tropsch synthesis [1]. The reaction has since become one of the important means of carbylation of hydrocarbon molecules. The hydroformylation process of olefins is also called "oxo synthesis", which refers to the reaction of olefins, carbon monoxide and hydrogen under the action of transition metal complexes to form an aldehyde or alcohol with one carbon atom more than the original molecule under certain pressure conditions [2]. Hydroformylation of olefins is a very important class of methods for the synthesis of aldehydes or alcohols. The reacted aldehydes and alcohols can be further processed into downstream products such as acids, esters and amines. These products can be used as surfactants, chemical plasticizers, silk additives, pharmaceutical intermediates and fragrances. Hydroformylation is slowly considered to be one of the most important industrial technologies due to its main economic value, utilization value and theoretical value. The catalyst for the hydroformylation reaction generally has a transition metal as a central atom [3]. However, the expensive price of metal limits the process of large-scale industrialization of hydroformylation. Later, people discovered the unique properties of ionic liquids, which can introduce functional groups containing specific functions into ionic liquids to create new catalysts [4-5].

In this paper, a novel 1-polyethylene glycol monomethyl ether-3-methylimidazoliumcarbonyl hydrazine ionic liquid catalyst was synthesized and used to catalyze the hydroformylation of octene. The optimum reaction conditions for catalyzing octene were found by experiment, and the yield and isomer ratio of the product were determined. Laid the foundation for "heterogeneity of homogeneous reaction for separation and recovery of precious metal catalysts".
2. Experimental

2.1. Materials and Instruments
Carbon monoxide(99.9%), toluene(AR), Hydrated antimony trichloride(Rh ≥ 39.0%), P-toluensulfonyl chloride(≥97%), NN-dimethylformamide(≥99.5%), Dichloromethane(AR), hydrochloric acid(37%), acetone(AR), Sodium iodide(≥99.0%), Pyridine(AR), Ether(AR), Nitrogen(99.9%), Argon(99.9%), Sodium bicarbonate(≥99.5%), Sodium thiosulfate(≥99.0%), Tetrahydrofuran(AR), PEG400(AR), Potassium hydroxide (≥85.0%), Petroleum ether(AR), Anhydrous magnesium sulfate(AR), Octene(AR), Syngas, Triphenylphosphine (99.0%), Cyclohexane(AR).

SP6800-A Gas Chromatograph was purchased from Shandong Lunan Ruihong Chemical Instruments Co., Ltd. (Shandong, China), Bruker TENSOR27FT-IR Infrared Spectrometer were supplied by Germany Brucker company. Stainless steel autoclave was purchased from Dalian University of Technology (Liaoning, China), FA1004 Electronic Balance were supplied by Shanghai Liangping Instrument Co., Ltd. SHB-III Circulating Water Multipurpose Vacuum Pump and DF-101S collector constant temperature heating magnetic stirrer was bought from Zhengzhou Great Wall Science Industry and Trade Co., Ltd. Schlenk vacuum operating line were supplied by Shanghai Tongxing Chemical Co., Ltd.

2.2. Synthesis method.

2.2.1. Synthesis of catalysts. The mPEG400, pyridine and TsCl dissolved in CH₂Cl₂ were added to the round bottom flask. The reaction was resumed at room temperature for 24 hours after 1 hour in an ice bath at 0°C, and then the reaction was continued for 30 minutes by adding appropriate amount of CH₂Cl₂. The product was extracted successively with saturated NaHCO₃ solution, HCl solution and distilled water. After drying with anhydrous magnesium sulfate and suction filtration by a vacuum pump, CH₂Cl₂ was removed by distillation under reduced pressure to give a white liquid.

NaI was reacted with mPEG tosylate dissolved in acetone at 60°C for 24h. After the reaction was completed, acetone was removed by atmospheric distillation, and an appropriate amount of CH₂Cl₂ and distilled water were added into, and the mixture was stirred at room temperature for 30 min. The products were extracted by distilled water with 5% Na₂S₂O₃ solution, saturated NaHCO₃ solution, then dried by anhydrous magnesium sulfate, filtered, and then removed CH₂Cl₂ by vacuum distillation.

N-methylimidazole, DMF and (mPEG) I were added to the autoclave. The mixture was stirred in carbon monoxide atmosphere at 80°C for 48 hours. After the reaction is completed, the autoclave is cooled to room temperature, and the product is washed repeatedly with fresh ether.

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\text{RhCl₃·nH₂O, freshly ground KOH powder and THF were placed in autoclave. After three times of replacement with argon, CO gas was filled to keep the pressure in the reactor at 1.0-2.0 MPa, and the reaction time was 24 hours at room temperature.}
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\text{RhCl₃·nH₂O + KOH + CO} \rightarrow \text{K[Rh₃(CO)₉]} + \text{K}_2\text{CO}_3 + \text{KCl} + \text{H}_2\text{O} \quad (2)
\]
Iodine 1-polyethylene glycol monomethyl ether-3-methylimidazolium ionic liquid, K[Rh₆(CO)₃] and THF were added to the argon-filled reactor and reacted at 28°C for 2 hours. After the reaction, the solvent was removed by atmospheric distillation under the protection of argon, and a red-brown viscous catalyst was obtained.

\[ \text{CH}_3 \]

2.2.2. Hydroformylation reaction. Hydroformylation of octene was carried out in a 75 mL autoclave. Triphenylphosphine, octene, n-heptane and 1-Polyethylene glycol monomethyl ether-3-methylimidazole carbonyl rhodium ionic liquid catalysts were added in turn. After boiling, check the air tightness of the device. The autoclave was first replaced with argon three times, and then charged with a certain pressure of synthesis gas, and then the autoclave was placed in a heating mantle to start the reaction, and the product was analyzed after the reaction was completed.

3. Results and Discussion

3.1. Characterization of ionic liquids

3.1.1. Structural characterization of ionic liquids

![Figure 1. IR spectrum of [CH₃O(CH₂CH₂O)ₙmim][Rh₆(CO)₃]](image)

As shown in Figure 1, the infrared spectrum of the polyether carbonyl hydrazine ionic liquid exhibits its methyl stretching vibration peak in the wavenumber range of about 3131 cm⁻¹, and the methyl bending of 1455 cm⁻¹ and 1390 cm⁻¹. Vibrating peaks, etc., indicate the presence of a methyl group on the imidazole ring; 2015 cm⁻¹, 1955 cm⁻¹, 1800 cm⁻¹, and 1731 cm⁻¹ are all carbonyl absorption peaks when assigned to [Rh(CO)₄]⁻ and [Rh₆(a mixture of CO)₁₅]⁻. At the 438 cm⁻¹ and 420 cm⁻¹ positions, weaker absorption peaks appeared, indicating the presence of Rh-CO and Rh-C, respectively, thereby further illustrating the presence of the tetracarbonyl ruthenium anion [Rh(CO)₄]⁻.

3.1.2. Physical Characterization of Ionic Liquids. The liquid range of most ionic liquids is larger than that of traditional solvents, and can reach up to 400°C. Since the ionic liquids synthesized by us are liquid at atmospheric pressure, the thermal decomposition temperature of ionic liquids is taken as the upper limit of their liquid range. In this paper, we performed thermogravimetric analysis on the
synthesized ionic liquid in the range of 50–600°C. The thermogravimetric analysis curve is shown in Figure 2.

Figure 2. The TGA curve of \([\text{CH}_3\text{O}((\text{CH}_2\text{CH}_2\text{O})_n\text{mim})][\text{Rh}_x(\text{CO})_y]\)

It can be seen from the thermogravimetric curve that the ionic liquid begins to decompose at around 267.73°C, that is, the thermal decomposition temperature is 267.73°C. It shows that the ionic liquid has good stability, and the reaction catalyzed by carbonyl ruthenium is lower than 200°C, so it can be applied to most of its carbonylation reactions.

3.2. Establishment of temperature-controlled two-phase system
Yang Yuchuan, Jin Lin et al.[6]. screened a three-component system with better "dynamic" loading by plotting the phase diagrams of PEG400/1,4-dioxane/n-heptane at different temperatures. Based on their ideas, we prepared the same volume of PEG400, 1,4-dioxane and n-heptane in a test tube, and then added an appropriate amount of polyether carbonyl hydrazine liquid to the test tube and place the test tube in the oil bath to heat up gradually.

Figure 3. Thermoregulated biphasic system of polyether carbonyl rhodium ionic liquid and PEG400,1,4-dioxacyclohexane and n-heptane

At room temperature, the polyether carbonyl hydrazine ionic liquid is in two-phase system with PEG400, 1,4-dioxane and n-heptane. The upper layer is n-heptane, and the lower layer is ionic liquid and PEG400/1,4-dioxane (See Figure 3.A). When the temperature rises to T=94°C, the two phases become miscible and become homogeneous (See Figure 3.B). When the temperature drops to room temperature, the homogeneous system becomes two phases again, the upper layer is n-heptane, and the lower layer is ionic liquid and PEG400/1,4-dioxane (See Figure 3.C).

Through this experiment, we can obtain two phases system of temperature control characteristics of "high temperature homogeneous, low temperature two phase" by polyether carbonyl hydrazine ionic liquid catalyst and PEG400/1,4-dioxane/n-heptane three components. The miscibility temperature (CST) of the two-phase system is about 94°C. This conclusion creates conditions for the separation,
recovery and reuse of precious metal catalysts.

3.3. Determination of the Optimum Reaction Conditions for Hydroformylation of Octane

3.3.1. Temperature

Table 1. Effect of Temperature on Octene Hydroformylation

| T(℃) | Conversion(%) | n | Yield (%) | Yield (%) | n/i |
|------|--------------|---|-----------|-----------|-----|
| 90   | 87.3         | 63.8 | 18.0       |            | 3.54 |
| 100  | 90.2         | 70.6 | 19.8       |            | 3.56 |
| 110  | 86.7         | 65.3 | 17.4       |            | 3.75 |
| 120  | 83.5         | 63.8 | 16.3       |            | 3.91 |

As can be seen from Table 1, the conversion of octene reached a maximum at a reaction temperature of 100°C. Both the normal aldehyde and the isomeric aldehyde have the highest yield at 100°C. The results show that as the reaction time increases, the selectivity of the reaction will continue to increase. So choose 100 °C for the best reaction time.

3.3.2. Pressure

Table 2. Effect of Pressure on Octene Hydroformylation

| PCO/H2(MPa) | Conversion(%) | n | Yield (%) | Yield (%) | n/i |
|-------------|--------------|---|-----------|-----------|-----|
| 2.0         | 0            | 0 | 0         | 0         | -   |
| 3.0         | 24.95        | 16.68 | 5.6    | 3         |
| 4.0         | 79.4         | 54.48 | 26.69 | 2.04      |
| 5.0         | 43.23        | 23.89 | 17.33 | 1.38      |

The experiment shows that the yield of normal aldehyde increases with the increase of pressure, and the yield of isoform aldehyde also increases with the increase of pressure. When the pressure of syngas is 4MPa, the conversion rate of octene The highest, but after increasing the pressure, the isomer ratio is reduced, and the selectivity of the reaction is reduced. Therefore, the optimum reaction pressure of 4MPa is selected as octene.

3.3.3. Reaction time

Table 3. Effect of Reaction Time on the Hydroformylation of Octene

| Time(h) | Conversion(%) | n | Yield (%) | Yield (%) | n/i |
|---------|--------------|---|-----------|-----------|-----|
| 3       | 64.7         | 39.6 | 18.3       |            | 2.16 |
| 4       | 79.4         | 50.4 | 20.6       |            | 2.45 |
| 5       | 83.5         | 60.8 | 19.9       |            | 3.05 |
| 6       | 81.2         | 55.1 | 18.0       |            | 3.06 |

It can be seen from Table 3 that the hydroformylation reaction of octene reached a maximum at a reaction time of 5h, and the yield of n-nonylaldehyde reached a maximum. It can also be seen that as the reaction time increases, the selectivity of the reaction also increases. So choose 5h for the best reaction time.

4. Conclusion
1-polyethylene glycol monomethyl ether-3-methylimidazoliumcarbonyl ruthenium ionic liquid catalyst was synthesized and characterized by Fourier-infrared spectroscopy IR to determine its
structure. Then check the physical properties through thermogravimetric and solubility analysis, and establish a temperature control system. Then the temperature-controlled two-phase system was applied to the hydroformylation catalytic reaction of octene. The effects of pressure, temperature and time on the catalytic reaction of octene hydroformylation were investigated. The suitable reaction conditions and reaction results were obtained: The pressure was 4.0MPa, the reaction temperature was 100°C, and the reaction time was 5h. The conversion of octene was 90.2%, and the yield of n-nonylaldehyde was 70.3%.

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