



Catalytic Hydrogenation of Alkenes using Rhodium Supported Catalysts

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Abstract This paper described the synthesis and characterized of rhodium supported on polystyrene-divinylbenzene copolymer used as heterogeneous catalysts for the hydrogenation of 1-hexene. The catalytic activity and selectivity of the new rhodium supported catalyst was studied and compared with homogenous ones.

The mechanism of the reaction was the same for both homogenous and heterogenous supported catalytic system, thus the rate constant were determined and found to be 0.800 and 0.090 $l\ mol^{-1}\cdot sec^{-1}$ for both system respectively. A wide range of polymer supported catalysts have been screen in the use of rhodium supported catalysts and their thermal stability was studied (1-7).

Keywords Catalytic Hydrogenation, Alkenes, Rhodium Supported Catalysts

Introduction

Hydrogenation meaning treatment with hydrogen which a chemical reaction between molecular hydrogen(H_2) and another compounds or elements, usually in the presence of catalyst such as nickel, platinum, palladium or rhodium. The process commonly employed to reduce unsaturate organic compounds.

Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to a molecule, often an alkenes or alkynes. Catalysts are required for the reaction to be usable, non- catalytic hydrogenation take place only at very high temperature. Hydrogenation reduces double and triple bonds in hydrogenation [6].

Previous work show that a wide range of polymers have been screen for their use in the context of support [8-10]. The more conventional supports include many halogenated and hydroxylated polymers such as polyvinylchloride and silica, for which substitution reactions are used to introduce pendant donor groups (i.e. phosphine, arsines and amines) were reported [11,12].

In this paper reports the synthesis, catalytic and mechanism of both homogenous and supported rhodium catalyst for the hydrogenation of 1-hexene.

Experimental

A sample of rhodium trichloride ($RhCl_3\cdot 3H_2O$) was obtained from Jhonson-Mathey company Ltd. Tris (triphenyl phosphine) chloro rhodium(I) was prepared by published method [7] and gave a satisfactory elemental anslysis. Polystyrene- divinylbenzene complymers obtained from Rhom and Hass was washed with pure methanol as previously described in the literature [13,14].

Diphenylphosphnyation of the resin



To the resin (0.14 mole) which left for two hours in THF (200 ml) to swell, a solution of LiPph_2 (0.278 mole) in THF (300 ml) was added slowly over a period of 1 hr. The mixture was reflux for 16 hr. A deoxygenated saturated solution of ammonium chloride (150 ml) was added to the mixture and stirred for 6 hrs. The yellow beads were washed with distilled water containing trace of HCl distilled water and THF respectively. The resin was dried for 3 days at 60 °C under vacuum.

Calculated	C=8.5%	H=6.6%	Cl=0	P=9.7 (based on 100 % phosphination)
Found	C=76.9%	H=6.4%	Cl=4.3%	P=8.5%

Reaction of $\text{RhCl}(\text{Pph}_3)_3$ with phosphynated polystyrene

To the phosphynated resin (0.125 mole of phosphine) in 100ml deoxygenated of toluene was added under nitrogen atmosphere to a solution of $\text{RhCl}_3(\text{Pph}_3)_3$ (0.002 mole) dissolved in toluene. The mixture was reflux with stirring for 4hr. The reaction product was filtered and soxhleted in deoxygenated toluene under nitrogen pressure for 4hrs. The product was dried for 24hr. at 60°C under vacuum to yield orange product rhodium content was 0.4% by weight.

Hydrogenation Experiment

The supported catalyst was placed in a reactor with magnetic stirring bar. The reactor was then connected to a hydrogenation apparatus [11]

Readings of hydrogen uptake were made over certain period of time at conventional intervals.

For the hydrogenation of 1-hexene (0.138 mole), 0.2 g of the supported catalyst was used with 30 ml of dry benzene as a solvent.

Result and Discussion

Electron spectroscopy for chemical analysis (ESCA)

The complex $\text{RhCl}(\text{Pph}_3)_3$ supported on phosphinated resin was submitted for analysis of rhodium 4s,3p and 4p orbitals by ESCA. The supported catalysis indicates the presence of rhodium species. Binding energy for 4s of 74.0eV and 497.0eV and 49.6eV for 3p and 4p respectively.

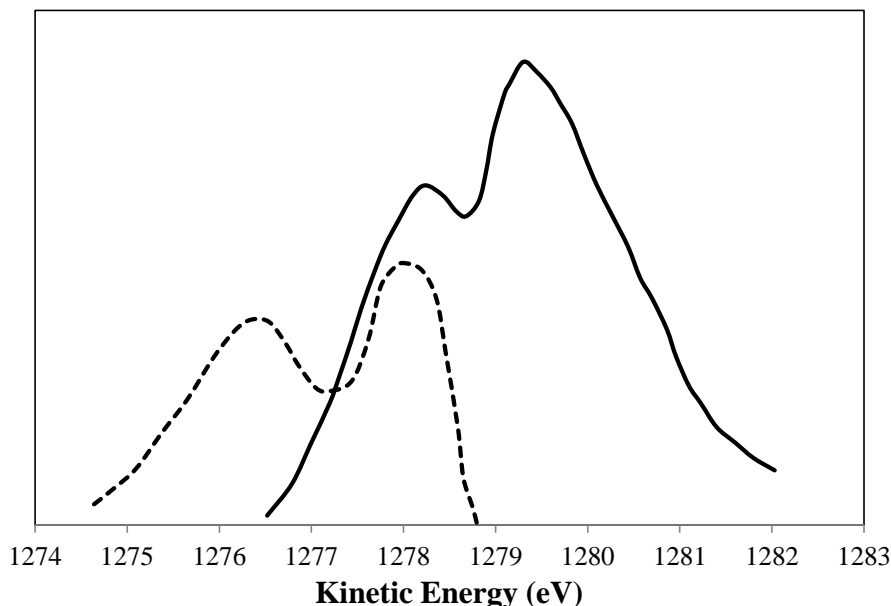
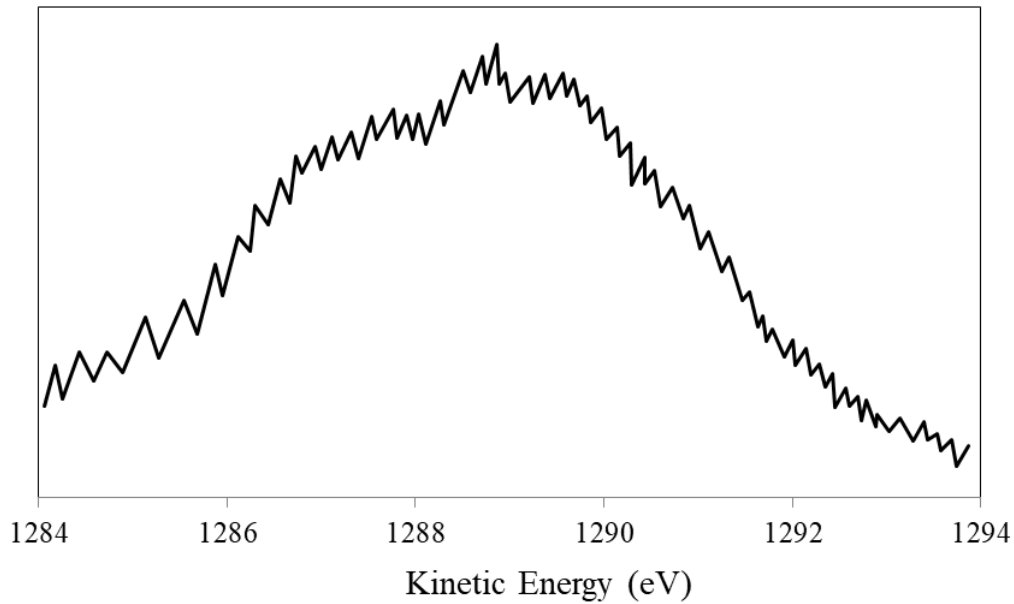


Figure 1 (a): ESCA spectrum of 2p orbital $\text{RhCl}(\text{Pph}_3)_3$ polystyrene (black) and polystyrene (dashed) sample (Calibrant carbon 1s. K.E. = 1192.2 eV, B.E. = 285.0 eV).

The ESCA experiment did, however, provide some interpretable results for example the analysis of chlorine 2p with $\text{RhCl}(\text{Pph}_3)_3$ supported on the phosphynated polystyrene resin (fig.1) show the ESCA spectrum in this regions.





The rate expression for hydrogenation of olefin by the homogeneous hydrogenation rhodium complex at 25 °C and 1 atm is [15]

$$\text{Rate} = \frac{K'' K_1 [\text{H}_2] [\text{S}] [\text{Rh}]}{1 + K_1 [\text{H}_2] + K_2 [\text{S}]}$$

Where [H₂] concentration of hydrogen in the solvent

[S] concentration of 1-Hexene (mole/l)

[Rh] concentration of rhodium complex (mole/l)

The proposed mechanism is shown in the following reaction scheme:

The rate expression rearrangement in terms of the hydrogen uptakes.

$$V = V_{\infty} (1 - \exp^{-(A+B)V/F})$$

Where V = volume of hydrogen uptake at STP in ml

V_∞ = volume of hydrogen uptake at t = ∞

$$A = \frac{K'' K_1 [\text{H}_2] [\text{S}] [\text{Rh}]}{1 + K_1 [\text{H}_2] + K_2 [\text{S}]}$$

$$B = \frac{K_2}{1 + K_1 [\text{H}_2]}$$

F = concentration factor to convert hydrogen uptake to a substrate concentration.

$$K_1 = 4.0 \times 10^3 \text{ (l/mole)}$$

$$[\text{H}_2] = 2.5 \times 10^{-3} \text{ (mole/l)}$$



Catalytic activity of the homogenous and the supported catalysts

The catalytic activity of the homogenous catalysts are studied as a function of 1-hexene concentration and temperature. The selectivity of the supported catalyst was investigated. Fig (2) shows plot of hydrogen uptake versus time on the hydrogenation of 1-hexene by rhodium supported and rhodium complex catalysts.

As can be seen from fig (2) the rate expression of supported catalyst fit the same rate expression of homogenous. The other rate value constant (fig 2) were obtained by analyzing the rate by analyzing the rate data (see Eq.1) for both homogenous and supported rhodium catalysts which were found 0.800 and 0.090 $\text{l mol}^{-1}\text{sec}^{-1}$ respectively. So it may be concluded that the attachment of the catalyst to the polymer did not change the mechanism of the reaction.

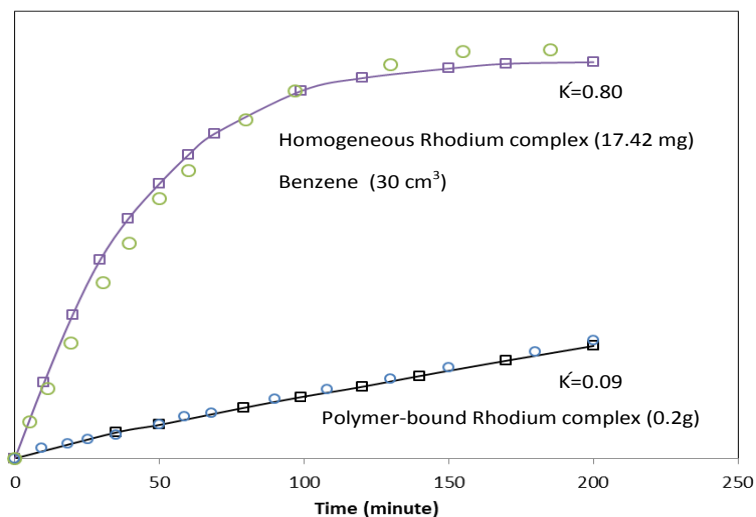


Figure (2): Hydrogenation of 1-hexene (0.318 M) catalyzed by the polymer-bound Rhodium catalyst and the equivalent amount of homogeneous rhodium complex at 25 C°. Experimental (○) and calculated (□).

Effect of temperature

In order to examine the temperature effect on the activity and selectivity of the catalyst the hydrogenation reaction was studied in the temperature range 15-45 °C. In such temperature range all runs exhibit the standard Arrhenius equation dependency (Fig. 3 and 4). The order of energies for both systems are in the same order of the reaction ($E_{\text{heter.}}=9.35$ and $E_{\text{homo}}=8.33$ Kcal/mol

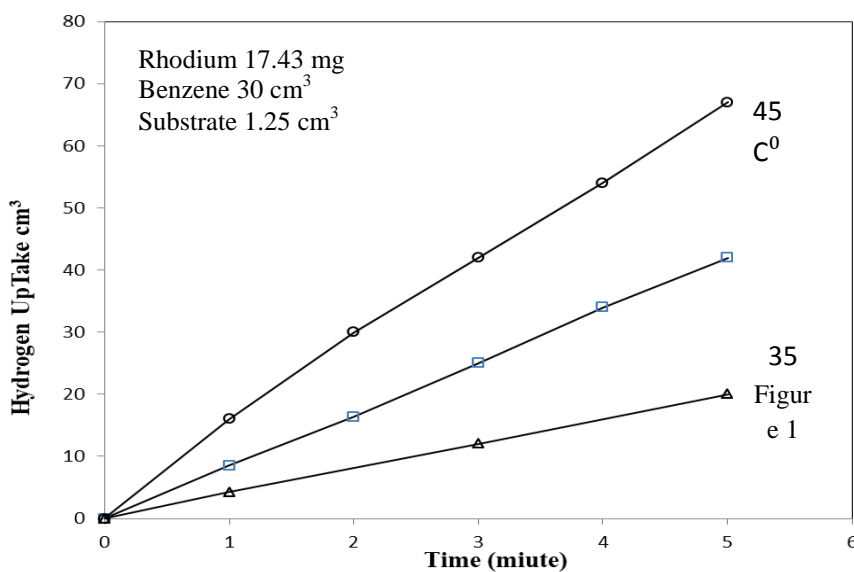


Figure (3): The effect of temperature the on initial rate of homogeneous Rhodium complex



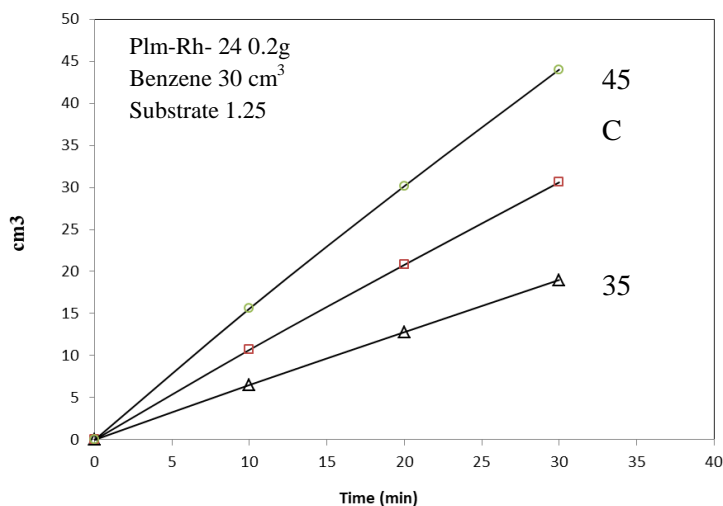


Figure (4): Effect of temperature on initial rate of hydrogenation of 1-hexene by the polymer-bound

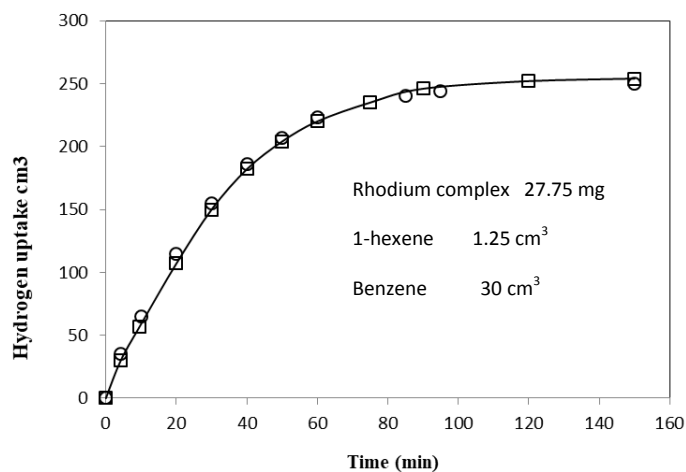


Figure (5): Hydrogenation of 1-hexene by homogeneous Rhodium complex at 25 °C. First run (□) and second run (○).

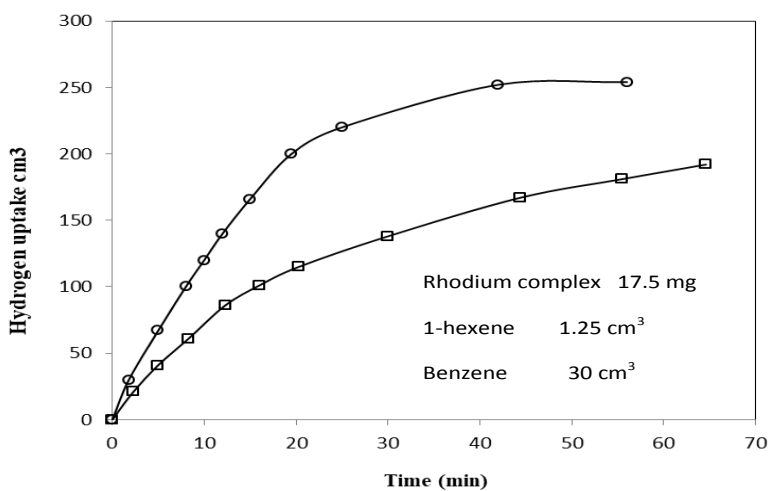


Figure (6): Hydrogenation of 1-hexene by homogeneous Rhodium complex at 45 °C (sequential run). First run (□) and second run (○).



Fig. (5 and 6) show the comparison of the catalytic activity of homogenous rhodium complex at 45^oC in sequential runs at 25^oC, the activity of the homogenous catalyst remains constant whereas by 50% at 45^oC. This may be attributed to the thermal deactivation of the catalytic was much less in the rhodium supported catalyst (Fig 7). It likely that aggregation might be prevented by rigidity of the resin matrix of the heterogeneous system.

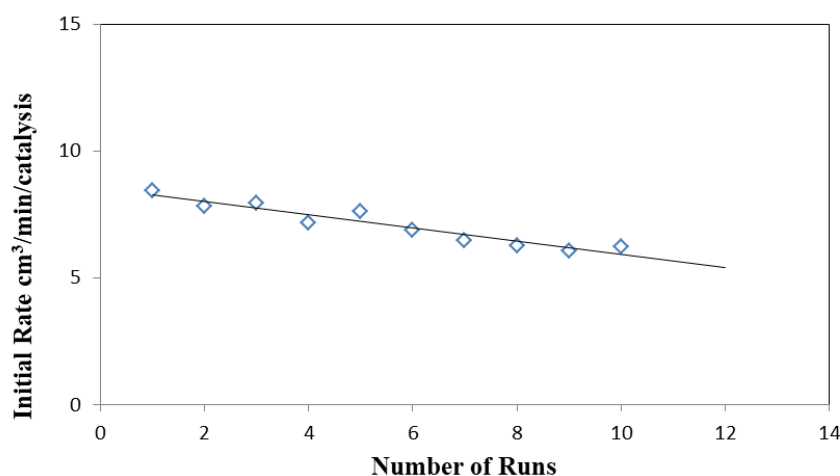


Figure (7): Effect of catalyst service on the activity of the polymer-bound rhodium complex at 45 C°.

Conclusion

The study of hydrogenation capabilities of the rhodium supported catalyst revealed the following characteristics:

- The kinetic comparison of activities of homogenous and supported catalyst indicates that the mechanism of the reaction were the same for both homogenous and supported catalyst.
- The selectivity remains unchanged.
- The rhodium supported catalyst was more thermally stable than the Homogenous ones.

References

- [1]. British Patents: 1,227 736; 1,312 611; 1,342, 876.
- [2]. Dialzman, D. Tomanova & J. Hetflejs, Collect, om., 39, 123, (1974).
- [3]. Hudhck, Milos, Amer. Chem. Soci. p.429, ISBN 0-8412-3344-6 (1996).
- [4]. Topics in Catalysis Vol. 34, No. 5, (May 2005).
- [5]. Chemical Society Reviews, 40(7), P. 3703-3727 (July 2011).
- [6]. H. Campo, J.B. Belmare etc., J. RSC Advance Vol. 6, (2017).
- [7]. J. L Oiaq, Z. Lang, R. Zou and Y. Zhao, Advance Material, Vol. 29, Issue 30 (Aug. 2017).
- [8]. N.D.A. Touma Aljabiri, Ph. Thesis, UMIS, Manchester, England, (1978).
- [9]. J.A. Osbern, F.H. Jardine & G. Wilkinson, J. Chem. Soci. A, 1711, (1966).
- [10]. L.A. Oro, M. Campo and E.M. Sweet, Molecular Catalyst, 39(3), (1987).
- [11]. R.H. Grubbs, L.C. Kroll and E.M. Sweet, J. Macromol Sci., A7, 1047 (1973).
- [12]. M. Capca & J. Helflejs, Collect. Czech, Comm., 39, 154, (1974).
- [13]. H. Bruner & J.C. Bailar, L. Inor. Chem., 12, 1465, (1973).
- [14]. L.D. Rollman, Inorgan. Ch im. Acta. 6, 137, (1972).
- [15]. J.A. Osborn, F.H. Jardine and G. Wilkinson, J. Chem. Soc., (A), 1711 (1966).

