

Hydroformylation of 1-hexene using Rh/TPPTS complex exchanged on anion exchange resin: kinetic studies

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Abstract

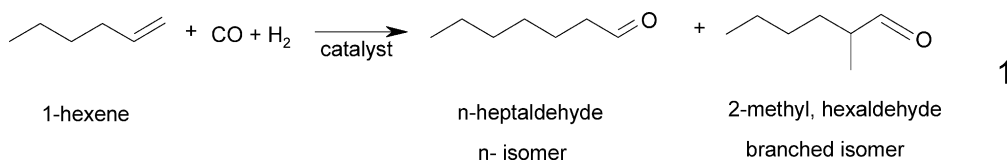
The exchange of the Rh/Triphenylphosphine trisulfonate sodium [TPPTS] complex on to an anion exchange resin results in a stable heterogenized catalyst for the hydroformylation of alkenes. The kinetics of hydroformylation of 1-hexene using Rh/TPPTS complex exchanged on anion exchange resin to Amberlite IRA-93 has been investigated for the first time. The rate of the reaction was found to be dependent on the partial pressure of hydrogen and 1-hexene concentrations with a first order. A maximum in the rate with increasing partial pressure of carbon monoxide was observed. A rate model has been proposed which predicts the observed rate data within reasonable error. The activation energy was found to be 84.37 kJ/mol.

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Keywords: Hydroformylation; Kinetics; Heterogenized catalyst; Ion-exchange resin; Rhodium

1. Introduction

The hydroformylation reaction is one of the most important industrial processes exclusively relying on homogeneous catalysis. This process produces the aldehydes by interaction of olefins with syngas in the presence of catalysts as shown below.



The application of water-soluble catalysts for hydroformylation reaction has been a major development in oxo technology [1]. However, due to problems associated with the solubility of the substrates in aqueous media, the application of this technology in commercial practice has been restricted to propylene and butene hydroformylation [2]. Heterogenization of the precious metal catalysts onto numerous supports has been envisaged, for more productive reactions and effi-

cient catalyst product separation [3]. The binding of the active metal complexes to ion exchange resins has been one such proposition [4]. In this paper, we report on the kinetics of hydroformylation of 1 hexene using Rh/Triphenylphosphine trisulfonate sodium (TPPTS) complex exchanged on to Amberlite IRA-93 Anion exchange resin.

2. Experimental

2.1. Materials

RhCl₃ was obtained from Ms Aldrich, CO and H₂ were obtained from Specialty Gas Co., India. TPPTS was synthesized from triphenyl phosphine and oleum by a well-documented procedure [5]. The water-soluble catalyst was prepared by ex-

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Nomenclature

D	concentration of 1-hexene (kmol m^{-3})
k	intrinsic rate constant ($\text{MPa}^{-2} \text{s}^{-1}$)
K_b	constant (MPa^{-1})
K_d	constant ($\text{m}^3 \text{kmol}^{-1}$)
P_A	partial pressure of hydrogen (MPa)
P_B	partial pressure of carbon monoxide (MPa)
R	rate of hydroformylation reaction ($\text{kmol m}^{-3} \text{s}^{-1}$)
ϕ_{\min}	sum of the squares of the error between the predicted and experimental rates

change method. The anion exchange resin Amberlite IRA-93 used for this purpose was obtained from Fluka, Switzerland.

2.2. Procedure for preparation of the resin catalyst

The Amberlite IRA-93 resin was first wetted with water and washed with 10% HCl. The chloride form of resin was then subsequently converted to the Triphenylphosphine trisulfonate [TPPTS] form by exchange with a 15% solution of the TPPTS sodium salt. The resin was washed thoroughly with distilled water followed by ethanol and then dried.

Prior to the reaction a known quantity of the dry resin in TPPTS form was added to a solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ in toluene (known concentration of Rh), under stirring. The rhodium was taken up by the TPPTS by complexation, with a consequent decolorization of the toluene. The analysis of toluene for Rh content showed a Rh concentration of <0.1 ppm, indicating that all the rhodium was complexed with the resin bound TPPTS. This resin was then washed with ethanol, and taken for reaction. The catalyst used for this study had a Rh content of 2.106 mg per g of dry resin.

2.3. Apparatus and procedure for high pressure reactions

The reactions were carried out in a 300 ml high-pressure stainless steel reactor manufactured by Parr Instrument Co., USA. This reactor was fitted with a transducer for monitoring of pressure, a temperature control with automatic heating and cooling, and a magnetic stirrer with variable speed. A reservoir filled with syngas was connected to the reactor via a constant pressure regulator. This enabled continuous feeding of the syngas from the reservoir, as per the consumption in the reactor, while maintaining the pressure in the reactor constant. The reaction was monitored by observing the pressure drop in the reservoir. For the reaction, the reactants and catalyst were charged into the reactor and the reactor was flushed with nitrogen and syngas. Following this the reactor and contents were heated to the desired temperature under low stirring (200 rpm). Once the temperature was attained the

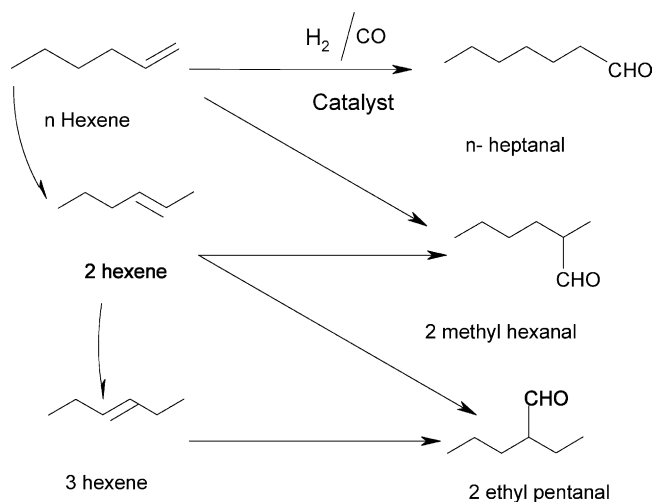
syngas ($\text{CO}:\text{H}_2$, 1:1) and CO or H_2 as required were pressurized into the reactor. The reaction was started by increasing the agitation speed to 1000 rpm. The gas consumed by the reaction was made up by a continuous addition of syngas ($\text{CO}:\text{H}_2$, 1:1) from the reservoir, wherein the pressure was monitored with time. During the course of the reaction, samples were withdrawn periodically and analysed by GC for reactant and products. For kinetic measurements, the reactions were conducted for fixed time duration, whereas for the screening study the reactions were conducted to high levels of conversion of 1-hexene. At the end of the reaction the autoclave was cooled and final samples were taken for analysis and confirmation of the mass balance.

The analysis of the products and reactants was done using GLC-HP 6890, on a HP-5 capillary column programmed between 33 and 290 °C.

3. Results and discussion

3.1. Preliminary reactions

A few reactions were taken to assess the feasibility of this catalyst for the hydroformylation of hexene-1. The main reactions observed were the formation of the normal and branched aldehydes, along with the isomerisation of hexene. The reactions are presented below.



Scheme for hydroformylation of 1-hexene

The analysis of the contents of the reaction indicated that the absorption of the syngas was commensurate with the formation of aldehydes and the consumption of olefins for the hydroformylation products. Since the role of the solvent is extremely important for this reaction from the point of view of selectivity to aldehyde as well as affecting the swelling characteristics of the resin/catalysts numerous solvents were screened to assess their influence on activity and selectivity to the reaction. The results are presented in Table 1.

A major side reaction with this catalyst was the isomerisation reaction, which occurred to the extent of $\sim 58\%$ in

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