



Hydroformylation of propene heterogeneously catalyzed by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ encapsulated in to hexagonal mesoporous silica—Parametric variation and mass transfer study

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ABSTRACT

An in situ encapsulated $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ in to the pores of hexagonal mesoporous silica (HMS) acting as nanophase reactors, was investigated for the catalytic hydroformylation of propene. The encapsulated catalyst (Rh–HMS) was synthesized and characterized by PXRD, FT-IR, surface area measurements and TEM. The catalyst was effectively active with 99% conversion of propene and 100% selectivity to aldehydes. The effects of reaction parameters: temperature, partial pressure of CO and H_2 , amount of catalyst and $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ to TEOS ratio on conversion, selectivity and rates were investigated in detail. The rates determined in term of the formation of aldehydes were found to be first order with respect to hydrogen pressure. Catalyst showed first order dependence towards its lower amount. CO pressure variation showed positive order towards lower pressure and inhibition at higher pressures. The investigated mass transfer effects on the kinetics indicated that the reaction runs with negligible mass transfer limitations. The heterogenized Rh–HMS catalyst was effectively recycled for six times.

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1. Introduction

Hydroformylation of olefin is one of the industrially important homogeneously catalyzed reactions [1] and nowadays, the world production approaches 10^7 tons/year [2] by this process. In this, nearly 86% of the total hydroformylation production capacity is based on the propene hydroformylation to give butanals (n- and iso-) as major products [3]. The use of n-butanol is chiefly for the production of C_8 -aldol products such as 2-ethylhexanal and 2-ethylhexanol, which are valuable intermediates for the production of dioctylphthalate, other plasticizers, coatings, adhesives, lubricants, alkyd resins and fine chemicals. Iso-butanol is converted to iso-butyl alcohol, neopentyl glycol, iso-butyl acetate, iso-butyric acid, iso-butyridene diurea, methyl iso-amyl ketone and various hydrogenation and esterification products. Monoisobutyrate synthesized by homo-aldol condensation of iso-butanol [4,5] is the most common coalescing agent (used at 0.5–2 vol%) in latex paints. Iso-butyl acetate and iso-butyridene diurea are used as a solvent for nitrocellulose coatings and for slow-release fertilizer respectively [6].

Industrially, hydroformylation process is performed under homogeneous conditions. However, homogeneous system has limitations of the separation and recycling of the catalyst. To overcome these drawbacks investigations are focused on the biphasic catalysis [7,8] and heterogenization of homogeneous catalysts [9–12]. The heterogenization of homogeneous catalysts was reported on the supports like SBA-15 [13], silicate membrane-activated carbon [14], hydrotalcites [15], zeolites [9] and alumina [16]. Hydroformylation of propene had been widely studied by homogeneous [17], heterogeneous [18] and two phase process with a water-soluble ligand modified catalyst [19].

Recently we have reported, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ encapsulated hexagonal mesoporous silica (HMS), as an efficient heterogeneous catalyst for hydroformylation of C_5 – C_{12} olefins [20,21]. Here the investigation is focused for the hydroformylation of lower and gaseous alkene, propene. In heterogeneous catalysts apart from the studies on conversion and selectivity, the detail investigations on the parametric variations, reaction kinetics and mass transfer effects play an important role. Though the reports on parametric studies are available for various substrates, the investigations on the kinetics of hydroformylation of propene over heterogeneous catalysts are paid less attention. Understanding the effects of diffusion leading to mass transfer constraints in heterogeneous conditions is more important and have pressing need to perform

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