Journal of Molecular Catalysis A: Chemical 400 (2015) 1–6

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Hydroformylation of dihydrofurans catalyzed by rhodium complex encapsulated hexagonal mesoporous silica

Munir D. Khokhar[b], Ram S. Shukla[a,*], Raksh V. Jasra[c,*]

[a] Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), G.B. Marg, Bhavnagar 364 002, Gujarat, India
[b] KAUST Catalysis Center (KCC), King Abdullah University of Science & Technology, 23955-6900 Thuwal, Saudi Arabia
[c] R&D Center, Vadodara Manufacturing Division, Reliance Industries Limited, Vadodara, Gujarat, India

ARTICLE INFO

Article history:
Received 13 August 2014
Received in revised form 30 October 2014
Accepted 24 January 2015
Available online 28 January 2015

Keywords:
Hydroformylation
Furans
Heterogeneous
Aldehydes
Hexagonal mesoporous silica

ABSTRACT

$HRh(CO)(PPh_3)_3$ encapsulated hexagonal mesoporous silica (HMS) is found to be an efficient heterogeneous catalyst for the selective hydroformylation of 2,3-dihydrofuran (2,3DHF) and 2,5-dihydrofuran (2,5DHF). The Rh-complex encapsulated *in situ* in the organic phase of template inside the pores of HMS was found to act as nano phase reactors. Conversion of 2,3-DHF and 2,5-DHF and selectivity of the corresponding aldehydes were thoroughly investigated by studying the reaction parameters: catalyst amount, substrate concentration, partial as well as total pressure of CO and H_2, and temperature. The selectivity for the formation of tetrahydrofuran-2-carbaldehyde (THF-2-carbaldehyde) from the hydroformylation of 2,3-DHF was found to be more than the selectivity of the formation of tetrahydrofuran-3-carbaldehyde (THF-3-carbaldehyde) from 2,5-DHF. The reaction paths are suggested and discussed for the selective formation of the corresponding aldehydes. The catalyst was elegantly separated and effectively recycled for six times.

1. Introduction

Furan and its derivatives have enormous potential applications and used as a chemical building blocks for the production of fine chemicals, pharmaceutical intermediates and pesticides [1–4]. The major furan based drugs being manufactured in pharmaceutical industries are ranitidine, prazosin, furosemide, cefuroxime, sulphamethoxazole and cefoxtin [5–9]. The important uses of these drugs are curing hypertension and congestive heart failure. Furan has a remarkable importance in the preparation of natural as well as synthetic pesticides because furan molecule is the key intermediate in the natural pesticide known as wyerone [10]. Pyrethrin [11] is another important pesticide among furan based pesticides. Intermediates for these products can be obtained by functionalizing the furan side chain selectively in the second position by utilizing various reactions like catalytic hydrogenation, hydroformylation, hydroformamination and oxidation routes. The literature is scanty for the functionalization of second position of the side chain of furan *via* catalytic hydroformylation in which rhodium complex is used as a catalyst along with syn-gas in homogeneous conditions [12–14].

Hydroformylation of furans [15] to hydroxymethyl tetrahydrofurans have been reported in modest yield using $Co_2(CO)_8$ catalyst. In the hydroformylation reaction, rhodium complexes have been found to be better catalysts [16] than cobalt based catalysts. $HRh(CO)(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ complexes have been reported to perform as effective catalysts for the hydroformylation of dihydrofurans under homogeneous conditions [12]. Noteworthy investigation in the hydroformylation of 2,3-dihydrofuran (2,3-DHF) and 2,5-dihydrofuran (2,5-DHF) in liquid phase had been reported by Lapidus et al. [17].

Investigations on the selective introduction of formyl group on the second and third position of the tetrahydrofuran, starting from 2,3-DHF and 2,5-DHF, respectively, have been reported [18]. In these reactions the modifications have been made in the employed reaction conditions and the ligands. Homogeneous hydroformylation is known for high selectivity and is used in the syntheses of fine chemicals and derivatives. The main draw backs associated with homogeneous hydroformylation are the separation of products from the solvent, high separation and catalyst cost. Numerous efforts have been made in the field of hydroformylation wherein the precious metal containing catalyst can be recovered from the reaction mixtures [19–23].

* Corresponding authors. Tel.: +91 278 2567760; fax: +91 278 2566970.
E-mail addresses: rshukla@csmcri.org (R.S. Shukla), rakshvir.jasra@ril.com (R.V. Jasra).

http://dx.doi.org/10.1016/j.molcata.2015.01.027
1381-1169/

Wilkinson catalyst has remained the important homogeneous catalyst for the hydroformylation reaction, as it offers high activity and selectivity for the reaction [24,25]. In our wide research programme on utilization of carbon monoxide in recent investigations, rhodium based catalysts were heterogenized and were found to be effective catalysts for hydroformylation [26–33] and hydroaminomethylation [34,35]. Immobilization [36] is one such route which can help the homogeneous catalyst to stay inside the porous materials and help prevent leaching or loss. Rhodium complex encapsulated into the mesopores of hexagonal mesoporous silica was found to act as nanophase reactor [26,37] in the catalytic hydroformylation of the double bond of the linear C_5–C_{12} alkenes under heterogeneous conditions. The main advantages in using HMS are its large wall thickness, small scattering domain sizes, complementary textural mesoporosities and thermal stability [38].

In the present paper, the work was carried out to investigate the performance of $HRh(CO)(PPh_3)_3$ encapsulated hexagonal mesoporous silica ($HRh(CO)(PPh_3)_3$–HMS) catalyzed heterogeneous hydroformylation of 2,3-DHF and 2,5-DHF, which are heterocyclic and important for pharmaceutical intermediates and pesticides. The catalyst is investigated in detail and the reaction parameters such as catalyst amount, total as well as partial pressure of CO and H_2, substrate amount and temperature effect on the hydroformylation were studied.

2. Experimental

2.1. Synthesis of the catalyst

Complex $HRh(CO)(PPh_3)_3$ [39], hexagonal mesoporous silica (HMS) [38] and the catalyst, $HRh(CO)(PPh_3)_3$ impregnated into HMS ($HRh(CO)(PPh_3)_3$–HMS) [26] were synthesized and characterized (see Supplementary information; Fig. S1–S7) by the reported procedures. The precise descriptions of their synthesis are as follows.

2.1.1. Synthesis of $HRh(CO)(PPh_3)_3$ complex

A solution of $RhCl_3{\cdot}3H_2O$ (2.0 g, 7.6 mmol) in ethanol (70 mL) was added to a refluxing solution of triphenylphosphine, PPh_3 (12 g, 46.0 mmol) in ethanol (300 mL). After 2 min, aqueous formaldehyde (10 mL) was added drop wise and the solution turned yellow with the formation of *trans*-$RhCl(CO)(PPh_3)_2$. Addition of sodium borohydride, (2.0 g) in ethanol to the above hot mixture yielded the yellow crystals of Rh-complex. The unreacted rhodium metal was removed by washing the yellow crystal with ethanol.

2.1.2. Synthesis of HMS

In a typical synthesis procedure 0.0027 mol of hexadecyl amine was dissolved in a mixture of 0.0909 mol of ethanol and 0.296 mol of deionised water. The solution was stirred at room temperature (RT) on a magnetic stirrer. To this stirring solution 0.01 mol of TEOS was added drop wise and mixture was kept for 1 h at RT. After 1 h, the white gel precipitate was formed, which was kept at RT for 18 h of aging. The material was filtered and washed with 1:1 (v/v) ethanol–water mixture and dried in vacuum at RT.

2.1.3. Synthesis of $HRh(CO)(PPh_3)_3$–HMS

For the synthesis of $HRh(CO)(PPh_3)_3$–HMS (Rh–HMS), the in situ encapsulation of the $HRh(CO)(PPh_3)_3$ into the HMS pores was done as follows. In a typical synthesis procedure, 0.0027 mol of hexadecyl amine was dissolved in a mixture of 0.0909 mol of ethanol and 0.296 mol of deionised water. The solution was stirred on a magnetic stirrer. To this stirring solution 0.07 mmol of $HRh(CO)(PPh_3)_3$ was added. To this suspension 0.01 mol of TEOS was added drop wise. Stirring was continued for 1 h and a pale yellow precipitate was formed, which was kept for 18 h for aging at RT. The yellow precipitate was filtered and washed with 1:1 (v/v) ethanol–water mixture and dried in vacuum at RT. The catalyst was calcined in air at 300 °C prior to its characterization. ICP analysis of $HRh(CO)(PPh_3)_3$–HMS gave 0.6 wt% of rhodium [26] in which the ratio of Rh-complex: TEOS was 3 wt%.

2.1.4. Hydroformylation and product analysis

The reaction was carried out in 100 mL bench top stirred reactor (Parr Reactors, USA; model No. 4843) having controlling unit and digital display for stirring speed and reaction temperature. In a typical experimental procedure, desired amount of the catalyst ($HRh(CO)(PPh_3)_3$–HMS) was added to 50 mL toluene as a solvent along with the substrate and *n*-decane as internal standard in the reactor. Carbon monoxide gas was fed before adding hydrogen to the system in order to avoid unnecessary hydrogenation of the substrate. Both the gases, CO and H_2 were fed to the required ratio followed by gradual increase in the temperature and the reaction was initiated by stirring the reaction mixture at 600 rpm. Liquid samples were withdrawn periodically through the sampling valve during the reactions and were analyzed using GC and GC–MS instruments equipped with flame ionization detector (FID). The GC oven temperature was programmed from 40 to 200 °C at the rate of 10 °C min^{-1}. N_2 was used as the carrier gas in GC and helium gas was used in GC–MS. Conversion of substrates and selectivity of the products was calculated from the % area of the GC report.

3. Results and discussions

3.1. Effect of the amount of the catalyst on the hydroformylation

Effect of the amount of the catalyst on the hydroformylation of 2,3-DHF and 2,5-DHF were studied at varied catalyst amount from 20 mg to 200 mg as depicted in Fig. 1. The conversion as well as selectivity gradually increases in both the cases. Maximum conversion of 99% with 90% selectivity of tetrahydrofuran-2-carbaldehyde (THF-2-carbaldehyde) was achieved with 200 mg of the catalyst in the case of 2,3-DHF. The conversion of 2,5-DHF to tetrahydrofuran-3-carbaldehyde (THF-3-carbaldehyde) attained saturation at 91% with 72% selectivity. The conversion and selectivity in the case of the hydroformylation of 2,3-DHF were comparatively higher than those of 2,5-DHF. The observed increased conversion of 2,3-

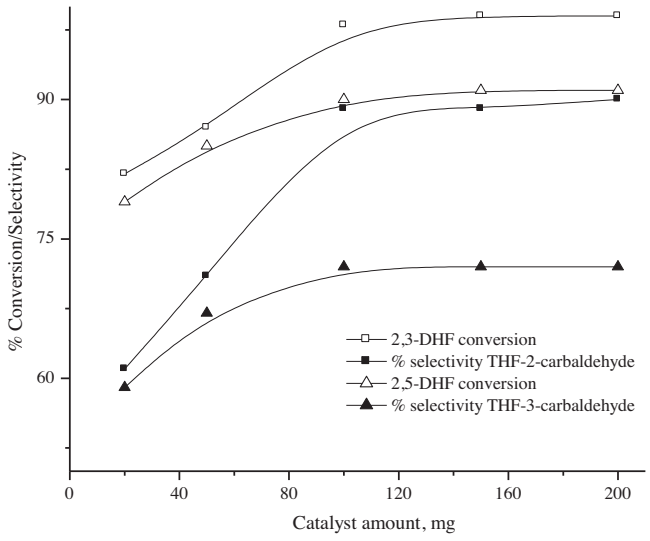

Fig. 1. Effect of the catalyst amount on the hydroformylation: substrate concentration = 9.07×10^{-2} M (2,3-DHF)/9.36×10^{-2} M (2,5-DHF), pCO = 15 atm., pH_2 = 15 atm., temp. = 80 °C, reaction time = 12 h.