Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Reductive-hydroformylation of 1-octene to nonanol using fibrous Co_3O_4 catalyst

Sachin S. Bhagade, Shivkumar R. Chaurasia, Bhalchandra M. Bhanage*

Department of Chemistry, Institute of Chemical Technology, N. P. Marg, Matunga, Mumbai 400019, India

ARTICLE INFO

Keywords:
Reductive-hydroformylation
Nonanol
Co_3O_4 nano-catalyst
Ligand and additive free
Recyclable catalyst

ABSTRACT

This work reports, reductive-hydroformylation of 1-octene to nonanol in the presence of fine fibrous cobalt oxide (Co_3O_4) nano-catalyst prepared via urea reduction method under phosphine-free and additive free condition. Co_3O_4 nano-catalyst was prepared by the wet chemical method and was characterized using various instrumental techniques like FEG-SEM, EDS, XRD, TPR and FTIR. The effects of various reaction parameters such as temperature, synthesis gas (CO/H_2) pressure/ratio, catalyst loading, solvent and time were studied. The reaction was successfully achieved in tetrahydrofuran (THF) as the solvent medium. This reaction believed to takes place through the generation of $HCo_x(CO)_y$ active catalyst species. The Co_3O_4 nano-catalyst could be recycled up to three consecutive cycles.

1. Introduction

The hydroformylation reaction is one of the largest scale applications of homogeneous catalysis in industry. Approximately 11 million metric tons of oxo chemicals are produced and consumed per year worldwide with an annual growth rate of 4% [1]. The active catalysts like Cobalt hydrocarbonyl [$HCo(CO)_4$] and phosphine modified Cobalt hydrocarbonyl [$HCo(CO)_3PR_3$], were generated in-situ from Co_2CO_8 and were intensively used as a first generation homogeneous oxo catalysts and still used in several oxo plants [2]. With the discovery of the first arylphosphine modified rhodium (Rh) catalyzed hydroformylation reaction by D. Evans et al. [3], rhodium based catalysts get considerable attention due to their excellent selectivity performance as compare to alkylphosphine modified cobalt catalyst. Along with this alternative transition metals like Ru, Pd, Pt, Ir, and Fe are also been reported in last few decades in hydroformylation reaction [4]. The use of these modified transition metals catalyst for hydroformylation reaction cycle is an attractive tool, however, although their applicability for the alcohol synthesis by Reductive-hydroformylation reaction is limited.

The selective synthesis of alcohols using hydroformylation-hydrogenation reaction sequence is an important process, which involves the direct conversion of alkenes to alcohols. The use of synthesis gas is more advantageous in such catalytic system and this also eliminates risk in the use of pure hydrogen for hydrogenation of aldehyde in a two-step reaction. These alcohols obtained *via* reductive- hydroformylation reaction are used as solvents, detergents building blocks, and plasticizers in the commercial chemical industry [5]. Till date, reductive-hydroformylation reactions have been well documented on modified cobalt, rhodium, ruthenium and palladium based metal catalysts [6]. A large-scale industrial application of Tributyl phosphine modified cobalt catalyst for alcohol synthesis by reductive hydroformylation in Shell industries is a well-known example of homogeneous reductive-hydroformylation [7]. Recently, G. Achonduh et al. reported a homogeneous reductive-hydroformylation of higher alkene using novel cyclic phosphine ligand modified cobalt catalyst [8]. Ligand modified rhodium metal catalyst acts as a platform for alcohol synthesis via hydroformylation-hydrogenation reaction [9]. Apart from the various phosphine ligand, the use of tertiary bidentate amine ligand for the synthesis of aromatic alcohol is demonstrated by L. Cheunge et al. [10]. Similarly, alcohol *via* reverse water gas shift hydroformylation-hydrogenation sequence has been studied well by Q. Liu et al. [11] using ruthenium/phosphite catalyst in presence of carbon dioxide. In 2006 halide anion promoted palladium catalyzed reductive hydroformylation was reported by D. Konya et al. [12] showing extended scope for synthesis of linear alcohol using internal alkene. To get the synergistic effect, a combination of two transition metals like Rh-Ru [13], Rh-Co [14] and Cu-Fe [15] for reductive-hydroformylation was also reported by few researcher.

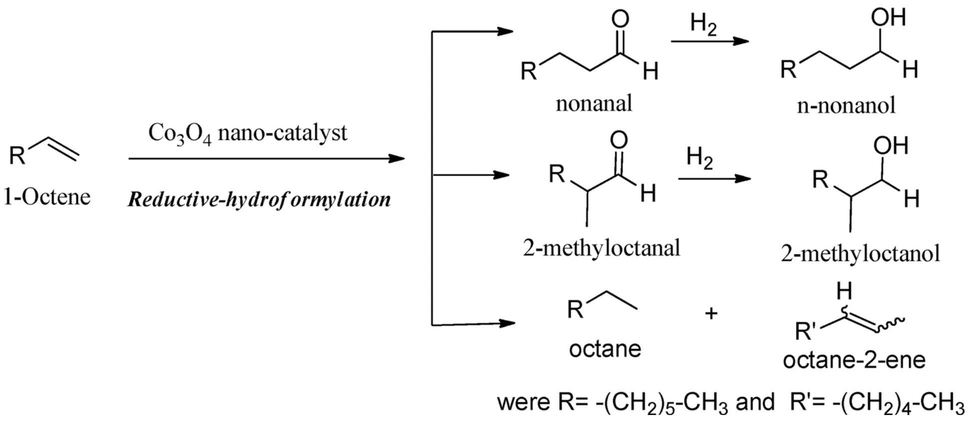
The use of heterogeneous or immobilized catalyst shows advantageous over homogeneous catalytic systems as they are easily recoverable and can be recycled. By considering the advantages of heterogeneous catalysis, synthesis of alcohol by Reductive hydroformylation of ethylene using supported cobalt carbonyl cluster is reported by J. Llorca et al. [16]. Albertus et al. [17] reported immobilized rhodium

---

* Corresponding author.
E-mail addresses: bm.bhanage@gmail.com, bm.bhanage@ictmumbai.edu.in (B.M. Bhanage).

http://dx.doi.org/10.1016/j.cattod.2017.08.022
Received 1 April 2017; Received in revised form 18 July 2017; Accepted 10 August 2017

Please cite this article as: Bhagade, S.S., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.08.022



Scheme 1. Reductive-hydroformylation of 1-octene.

metal complexes for the reductive-hydroformylation of 1-octene to 1-nonanol with the dual catalytical system. It is well known that Nano Co_3O_4-materials with different morphology is used as a gas sensor [18], catalyst [19] and in lithium-ion batteries [20]. Similarly, CoO nanomaterials act as an electrode material for electrochemical super capacitors [21]. Recently, Yuba ma et al. [22] developed a protocol for one pot synthesis of tricyclodecanedimethylol (TDDMO) using Co_3O_4 supported Au nanoparticles. They showed that there is a formation of $Co(CO)_x(PPh)_y$ like catalytically active complex on a Co_3O_4 surface which is assisted by Au nanoparticles supported on the surface of Co_3O_4. They have limitations like poor regio and chemo selectivity, the use of harsh reaction conditions, multistep synthetic procedures, the high cost of phosphine ancillary and difficulties in the recovery of a metal catalyst from the homogeneous reaction mixture. The applicability of these systems is not economical at a larger scale and more particularly for higher olefins. Hence, with our continuous interest in the synthesis gas application for fine chemical synthesis [23–26], herein, we wish to report a protocol for hydroformylation-hydrogenation of 1-octene to nonanol using fine fibrous Co_3O_4 nano-catalyst in absence of any co-catalyst or phosphine ligand (Scheme 1). Interestingly, this reaction was affected by different shape and sizes of Co_3O_4 nano-materials. Conversion and the selectivity towards desired product were found to be influenced by nature of solvent in the reaction medium and synthesis gas composition.

2. Experimental

2.1. Materials and instruments

All materials were procured from the reputed chemical supplier and were used without further purification. XRD (X-ray Diffraction) pattern of synthesized materials were recorded by Shimadzu XRD-6100 using CuKα-1.54 Å with scanning rate 2 theta (θ) per min and angle ranging from 20 (θ) to 80 (θ) having current 30 mA and voltage 40 kW. TPR (Temperature programmed reduction) profile was recorded with the help of TPDRO 1100 Instrument fitted with TCD(Thermo coupled detector) detector by passing 5% H_2 in argon at a rate of 10 °C/min, with temperature ramp from 30 to 800 °C. The FT-IR(Fourier Transform Infrared) spectra of synthesize nano-materials were recorded on Brucker Perkin Elmer-100 spectrometer in the wavelength range from 400 to 4000 cm^{-1}. Tescan MIRA 3 model with secondary electron (SE) detector were used for FEG-SEM (Field emission gunscanning electron microscopy) analysis using 10.0 kV. The EDS (Energy dispersive X-ray spectrum) was recorded on Oxford instrument (model 51-ADD0007). The yield of synthesized nonanol was confirmed by Perkin Elmer Clarus 400 GC GC (Gas chromatography) equipped with a flame ionization detector and a capillary column (elite-1, 30 m × 0.32 μm × 0.25 μm). The formation of product nonanol was confirmed by GC–MS(Gas Chromatography mass spectrometry). GC–MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness(df) = 0.25 μm) (column flow 2 mL min^{-1}, 70 °C to 240 °C at 10 °C/min rise) was used for the mass analysis of the products.

2.2. Catalyst preparation

(a) Synthesis of hexagonal Co_3O_4: 25 mL of distilled water was added to the 0.5 g of cobalt acetate hexahydrate and 0.25 g of β-cyclodextrin. To the above solution, 1 mL of liquid ammonia (25%) was added dropwise with continuous stirring, the resulting solution was then kept for sonication (30 kHz ultrasonic waves at the output power 5 s on and 5 s off mode) for 15 min. After sonication precipitate was separated by centrifugation and washed with distilled water and dried in an oven.
(b) Synthesis of fibrous Co_3O_4: fibrous shaped cobalt oxide nano-material was prepared by using method disclosed by M.M. Durano et al. [27b] with some minor modification. Typically Cobalt acetate hexahydrate (0.5 g) and urea (2.0 g) were dissolved in water and stirred using a magnetic stirrer for 20 min to form a pink color homogeneous solution. The resultant solution was then transferred to 100 mL round bottom flask and refluxed for 12 h. After cooling to room temperature, obtained product was washed with distilled water and dried at 80 °C. Finally, nano-Co_3O_4 material was then prepared by calcinating the resultant product at 400 °C for 4 h.
(c) Synthesis of flake type Co_3O_4: To 25 mL of distilled water 0.5 g of cobalt acetate hexahydrate and 0.25 g of β-cyclodextrin were added. To the above solution 1 mL of ammonia (25%) was added dropwise with continuous stirring and then kept for sonication for 15 min with the frequency of 60 kHz at the output power 5 s on and 5 s off mode. The resulting precipitate was then subjected to centrifugation and washed with distilled water and dried in an oven.

2.3. General procedure for reductive hydroformylation of 1-octene

In a typical experiment procedure, a 100 mL high-pressure reactor was charged with 1-octene (15 mmol), Co_3O_4(4 mol%) and 12 mL of dry THF. Then the reactor flushed three times with nitrogen to remove unnecessary gas contains and pressurized to 800 psi by CO/H_2 (1:2) gas. A reactor was then heated to 150 °C for 12 h with a constant stirring speed i.e. 700 rpm. After completion of the reaction time, the heater was stopped and the reactor was allowed to cool to room temperature. The existing synthesis gas was carefully released. The reaction mixture was then filtered using filter paper and the crude product was analyzed by gas chromatography and mass spectrometry [28].

2.4. Recyclability study

The consistent change in conversion and selectivity for product formation was observed from first to third recycle of nano-material