Chemical Engineering Journal 147 (2009) 366–372

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Hydrogen transfer from cyclohexanol to aromatic aldehydes catalyzed by heterogenized ruthenium(II) complexes bound to swellable polymer matrices

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ARTICLE INFO

Article history:
Received 24 September 2008
Received in revised form 17 November 2008
Accepted 25 November 2008

Keywords:
Hydrogen transfer
Cyclohexanol
Aromatic aldehydes
Ruthenium
Kinetics

ABSTRACT

Aromatic aldehydes can be reduced to corresponding alcohols by hydrogen transfer from cyclohexanol in the presence of Ru(II) complexes bound to swellable polymer matrices. The kinetics of the reaction has been measured between 100 and 140 °C. The process was shown to depend on the structure of aromatic aldehydes, on the concentrations of aldehyde and hydrogen donor, and on the amount of catalyst. The reaction proceeded efficiently in halogenated hydrocarbon solvents. The metal leaching and deactivation of the catalyst was studied. The metal leaching was different for subsequent catalytic runs and it is most pronounced in the first catalytic run. The IR spectra study for the catalyst deactivation showed that catalyst deactivation may be ascribed to the formation of metallic units bound to two carboxylate groups. This problem can be prevented by esterifying the groups. An apparent activation energy, Ea = 22 ± 1 kcal/mol was obtained, which suggests that the catalytic process involves predominantly a chemically controlled reaction. A general reaction mechanism and rate equation have been proposed.

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1. Introduction

Reduction of aldehydes and ketones to the corresponding alcohols is a valuable reaction in the pharmaceutical and chemical industry. The transfer hydrogenation can be accomplished with homogeneous, heterogeneous and water-soluble catalysts using different hydrogen sources such as isopropanol, formic acid derivatives and so on. The heterogeneous catalytic transfer hydrogenation has attracted widespread attention over the past few decades. Serious interest in these catalysts originated with efforts to develop catalytic systems displaying high activity, selectivity and reproducibility typical of homogeneous catalysts, combined with the easy separability and recovery characteristic of heterogeneous catalysts [1]. This is the direction and goals of researchers working on the polymer supported catalysts. We have reported the preparation of $RuH_2(PPh_3)_4$ immobilized on swellable polyacrylate matrices to provide heterogenized carboxylate-derivatives [2]. The ruthenium precursor, $RuH_2(PPh_3)_4$, was chosen for the anchoring reaction with the carboxylic groups of the swellable polymers giving either mono(carboxylato)- or bis(carboxylato)-species (Scheme 1).

The swellable polymer matrices are the crosslinked copolyacrylate and acrylamide. The supported ruthenium(II) complex catalysts (CCPAARu) have been used in the transfer hydrogenation of aldehydes. Hydrogen donors are formate salts and benzyl alcohol [3,4]. In the present work, the focus is on using the CCPAARu to catalyze hydrogen transfer from cyclohexanol to aromatic aldehydes (Eq. (1)). The CCPAARu catalyst contains 1.86 wt% of ruthenium. Hydrogenation of aromatic aldehydes to aromatic alcohol is not only an interesting organic reaction, but also a value added reaction, since generally aromatic aldehydes are cheaper than the corresponding alcohols.

(1)

2. Experimental

2.1. Materials

The solvents, bromobenzene (Aldrich, USA, 99%), chlorobenzene (Aldrich, USA, 99%), p-xylene (Aldrich, USA, 99%), nitrobenzene (Aldrich, USA, 99%) and 1,2-dichlorobenzene (Sigma–Aldrich, USA, HPLC grade) were distilled before use. The reagents, 2,6-dichlorobenzaldehyde (Aldrich, USA, 99%), 4-nitrobenzaldehyde

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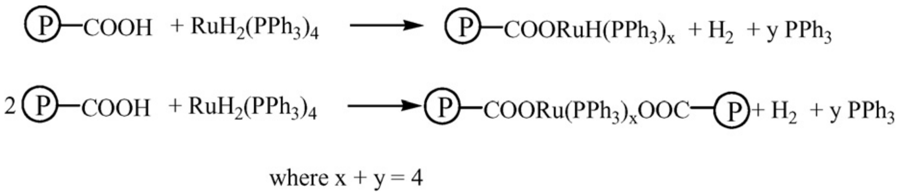
1385-8947/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.cej.2008.11.042



$$\text{Ⓟ–COOH} + RuH_2(PPh_3)_4 \longrightarrow \text{Ⓟ–COORuH}(PPh_3)_x + H_2 + y\,PPh_3$$

$$2\,\text{Ⓟ–COOH} + RuH_2(PPh_3)_4 \longrightarrow \text{Ⓟ–COORu}(PPh_3)_x\text{OOC–Ⓟ} + H_2 + y\,PPh_3$$

$$\text{where } x + y = 4$$

Scheme 1.

(Aldrich, USA, 99%), 4-bromobenzaldehyde (Aldrich, USA, 99%), p-tolualdehyde (Aldrich, USA, 97%), p-anisaldehyde (Aldrich, USA, 98%) and cyclohexanol (Aldrich, USA, 99%) were used as received. Ruthenium atomic absorption standard solution (Aldrich, USA, 990 ppm) was used as received.

2.2. *Synthesis of catalyst*

Details for the synthesis of the catalyst, CCPAARu (1.86 Ru%), are given in Ref. [2]. The particle size of CCPAARu is less than 250 μm.

2.3. *Gas chromatography (GC) analysis*

A PerkinElmer AutoSystem Gas Chromatograph coupled with 1020 PC plus was used for the analysis of hydrogen transfer reaction products, using a FID detector. The separations were accomplished with a 30 m × 0.322 cm column which was packed with DB-1 (100% polymethyl siloxane, 0.3 μm film).

2.4. *Direct current plasma analysis*

Ruthenium content in the CCPAA absorbent supported ruthenium complexes before and after reaction was determined by atomic emission spectrometer using SpectraSpan 7 Plasma Emission Spectrometer (SS-7) by ARL Fisons. Standards and polymeric samples for the DCP analysis were prepared according to the procedure described in Ref. [2].

2.5. *IR spectra analysis*

The infrared spectra of $RuH_2(PPh_3)_4$, naked superabsorbent (CCPAA) and superabsorbent supported Ru(II) (CCPAARu) complexes were obtained using a Nicolet 520 FTIR Spectrophotometer equipped with an IBM PC and Omnic software for spectra subtraction and areas calculations.

2.6. *Kinetic measurements*

Kinetic measurements were made by following the conversion of 2,6-dichlorobenzaldehyde to corresponding 2,6-dichlorobenzyl alcohol using GC. Typically, a nitrogen-flushed 25 ml flask equipped with a reflux condenser, two neoprene-capped side arms and a magnetic bar was immersed in an oil bath thermostated at 140 ± 1 °C. 0.113 g (0.129 M) 2,6-dichlorobenzadehyde, and 0.258 g (0.52 mM) cyclohexanol in 5 ml of 1,2-dichlorobenzene were added to the flask. After a temperature equilibration, 0.035 g (6.44×10^{-3} mmol ruthenium) CCPAARu was added. In order to eliminate the stirring rate effect, all the experiments were carried out at a constant stirring rate of 800 rpm. 0.4 μl samples were withdrawn periodically with the aid of a syringe and subjected to gas chromatographic analysis. Naphthalene (0.1000 g) was used as internal standard.

3. Results and discussion

3.1. *GC analysis of reaction products*

GC was used to monitor the transfer hydrogenation of 2,6-dichlorobenzaldehyde. The resulting chromatogram is show in Fig. 1. The products were also identified by GC–MS with a VG TRIO-1 Benchtop instrument. The spectra of the reactants and products fit well with the known compounds. It should be noted that although the product of the substituted benzyl alcohol, like benzyl alcohol, has hydrogen donor ability [4], the reaction (Eq. (1)) does not take place in the reverse direction, in other words, full conversions of the substrate can be obtained. This fact is interpreted by the explanation that cyclohexanone is more stable and it is difficult to be hydrogenated. Imai et al. [5] studied the hydrogen donating ability of some organic compounds to aldehydes. They found that cyclohexanol showed excellent hydrogen donating ability. The reason is the resulting dehydrogenation product, cyclohexanone, is relatively stable.

3.2. *Effect of solvent*

A correct choice of solvent is an important factor governing the activity of the catalyst in transfer hydrogenation reactions. Coordination of solvent to the catalyst in heterogeneous systems must be competitive with binding of hydrogen donors and hydrogen acceptors. If the coordinate link between solvent and catalyst is stronger than the binding of donor or acceptor, then transfer hydrogenation reaction is inhibited or stopped altogether. Several examples emphasize this solvent effect and a range of solvents

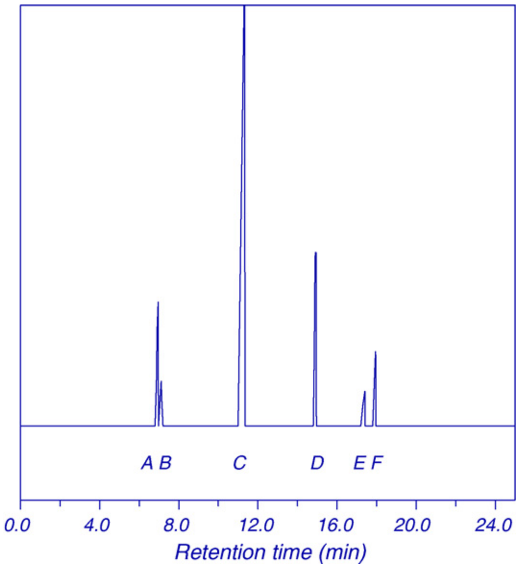


Fig. 1. Gas chromatogram of transfer hydrogenation of 2,6-dichlorobenzaldehyde. (A) Cyclohexanol; (B) cyclohexanone; (C) 1,2-dichlorobenzene; (D) naphthalene (internal standard); (E) 2,6-dichlorobenzaldehyde; (F) 2,6-dichlorobenzyl alcohol.