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

Z.S. Liu*, G.L. Rempel

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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, $Ea = 22 \pm 1$ 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.

Published by Elsevier B.V.

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

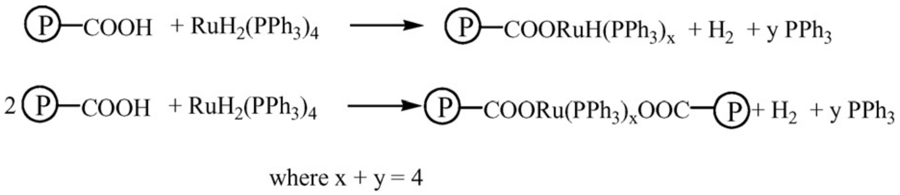
The solvents, bromobenzene (Aldrich, USA, 99%), chlorobenzene (Aldrich, USA, 99%), p-xylene (Aldrich, USA, 99%), nitrobenzene (Aldrich, USA, 99%) and 1,2-dichlorobenzene (Sigma–Aldrich, USA, HPLC grade) were distilled before use. The reagents, 2,6-dichlorobenzaldehyde (Aldrich, USA, 99%), 4-nitrobenzaldehyde

---

* Corresponding author. Current address: Food and Industrial Oil Research, National Center for Agricultural Utilization Research, Agricultural Research Service/U.S. Department of Agriculture, 1815 N. University Street, Peoria, IL 61604, USA. Tel.: +1 309 681 6104; fax: +1 309 681 6340.

E-mail addresses: kevin.liu@ars.usda.gov (Z.S. Liu), grempel@cape.uwaterloo.ca (G.L. Rempel).

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



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

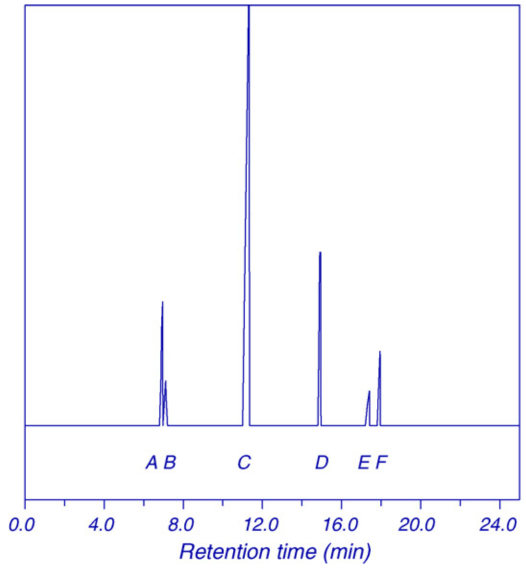


Fig. 1. Gas chromatogram of transfer hydrogenation of 2,6-dichlorobenzaldehyde. (A) Cyclohexanol; (B) cyclohexanone; (C) 1,2-dichlorobenzene; (D) naphthalene (internal standard); (E) 2,6-dichlorobenzaldehyde; (F) 2,6-dichlorobenzyl alcohol.

Table 1
Solvent effect in transfer hydrogenation.

Solvent	Dielectric constant (*T*, °C)	k' ($\times 10^3$ min^{-1} (140 °C))
1,2-Dichlorobenzene	9.93(25)	2.08
Bromobenzene	5.40(25)	1.91
Chlorobenzene	5.62(25)	1.01
Nitrobenzene	38.82(25)	0.29
Nitrobenzene	38.82(25)	0.32
p-Xylene	2.27(25)	0.43

should be a prime consideration [6]. Initial rates of the hydrogen transfer reaction from cyclohexanol to 2,6-dichlorobenzaldehyde in several halogenated and non-halogenated aromatic hydrocarbon solvents were measured. The reactants dissolved well in these solvents at the reaction temperature. The reaction was carried out at concentrations of 0.13 M 2,6-dichlorobenzaldehyde and 0.52 M cyclohexanol in 5 ml of a designated solvent. A catalyst amount of 6.44×10^{-3} mmol Ru of CCPAARu and a temperature of 140 °C were maintained for this series of runs. The results obtained are presented in Table 1. These results show that the reaction proceeded efficiently in halogenated hydrocarbon solvents with higher dielectric constants. The transfer hydrogenation reaction proceeds slowly in nitrobenzene. This may be due to possible coordination of nitrobenzene to the catalyst. Strongly coordinating nitrobenzene blocks coordination of reactants and makes transfer hydrogenation difficult, especially for more sterically hindered aromatic aldehydes. For the present kinetic study, 1,2-dichlorobenzene was used as a solvent because of the higher reaction rate.

3.3. *Effect of the structure of the aldehyde*

Several aromatic aldehydes were examined as hydrogen acceptors. The reaction was carried out at concentration of 0.13 M of the designated aldehyde and 0.52 M of cyclohexanol in 5 ml of 1,2-dichlorobenzene. A catalyst amount of 6.44×10^{-3} mmol Ru of CCPAARu and a temperature of 140 °C were maintained for this series of runs. The results obtained are summarized in Table 2. They show that electron-withdrawing groups enhance hydrogen transfer hydrogenation, while electron-donating substituents have a negative effect on the reaction rate. This trend was also observed in other transfer hydrogenation reactions with a hydrogen donor [3]. For the present kinetic study, 2,6-dichlorobenzaldehyde was chosen for all the experiments.

3.4. *Metal leaching*

The ruthenium content of the CCPAARu catalyst after reaction was determined by DCP analysis. The results are presented in Fig. 2. The metal leaching of the CCPAARu catalyst was different for subsequent runs and it is most pronounced in the first catalytic run. When fresh CCPAARu catalyst was used for a batch run, then washed, dried and reused, a significant decrease in the rate of reaction would be observed. The conversions of 2,6-dichlorobenzaldehyde catalyzed by fresh and recycled CCPAARu are presented in Table 3. The results show that the catalyst can be reused, however, the activity of the catalyst decreased much more than expected based on the metal loss due to leaching. The deactivation of catalyst will be discussed in a following discussion.

Table 2
Rate constants of transfer hydrogenation of some substituted benzaldehyde, ArCHO, from cyclohexanol catalyzed by CCPAARu.

Aldehyde	Temperature (°C)	k' ($\times 10^3$ min^{-1})
2,6-Dichlorobenzaldehyde	140	2.08
4-Nitrobenzaldehyde	140	1.12
4-Bromobenzaldehyde	140	0.53
p-Tolualdehyde	140	0.42
p-Anisaldehyde	140	0.19

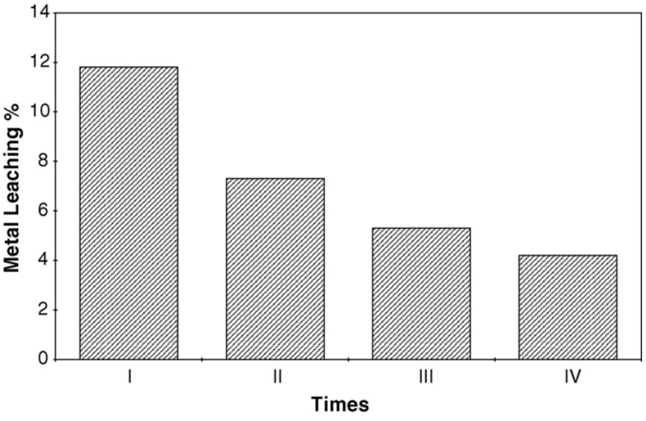


Fig. 2. Metal leaching of CCPAARu catalyst.

3.5. *Identifying the contributions of homogeneous catalyst in the overall transfer hydrogenation reaction*

If some portion of the ruthenium species is leached from the polymer supported catalysts in the system, the contributions of these species to the overall catalytic reaction are of importance in assessing the overall catalyst system. In other words, whether the catalysis is dominated by the heterogeneous catalyst or the homogeneous catalyst is a key question which needs to be addressed. The reaction was carried out with an initial 2,6-dichlorobenzaldehyde concentration of 0.13 M, a concentration of 0.52 M of cyclohexanol in 5 ml of 1,2-dichlorobenzene at 140 °C. A catalyst amount of 0.0009 g (0.78×10^{-3} mmol) of $RuH_2(PPh_3)_4$, which corresponds to 11.8% ruthenium leached from the CCPAARu catalyst (see Fig. 2) and 0.4 g acetic acid were added to the system in order to carry out the reaction under the existence of carboxylate ligand coordinator. The results show that conversion of 2,6-dichlorobenzaldehyde to 2,6-dichlorobenzyl alcohol catalyzed by $RuH_2(PPh_3)_4$ is only 6.6% at 24 h. However, the conversion of 2,6-dichlorobenzaldehyde to 2,6-dichlorobenzyl alcohol catalyzed by the CCPAARu catalyst is 90% at 24 h. Based on these results, it appears that the heterogeneous ruthenium species is the predominant catalyst for the transfer hydrogenation reaction.

3.6. *Catalyst deactivation study*

Although the metal leaching of the CCPAARu catalyst in the hydrogen transfer reaction from cyclohexanol to 2,6-dichlorobenzaldehyde was not in large amount, the activity of the catalyst showed a remarkable drop on the recycled application. The reason is probably due to the change of coordinator numbers to the metal unites. A comparison of IR spectra between fresh

Table 3
Conversion of 2,6-dichlorobenzaldehyde to 2,6-dichlorobenzyl alcohol catalyzed by fresh and reused CCPAARu catalyst (*T* = 140 °C).

Use of catalyst (cycle)	Initial Ru%	Reaction time (h)	Conversion (%)
1	1.86	24	90
2	1.64	24	50
3	1.52	24	39.8
4	1.44	24	28.3

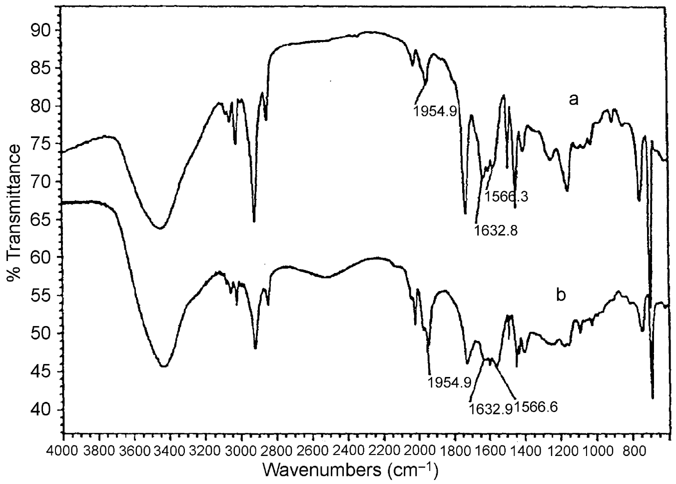


Fig. 3. IR spectra of fresh and recovered CCPAARu.

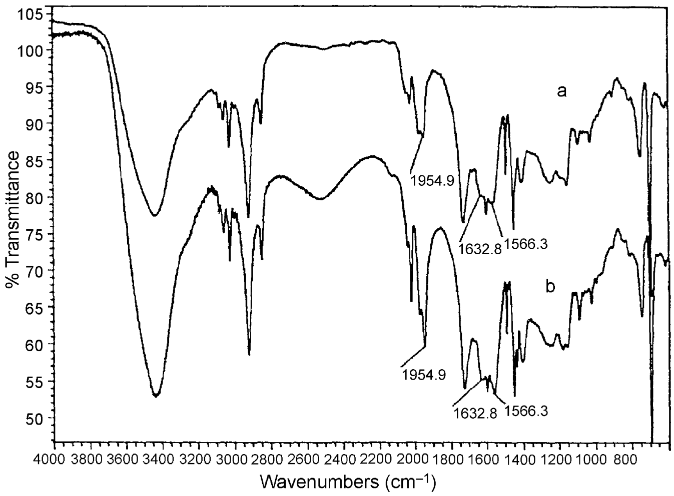


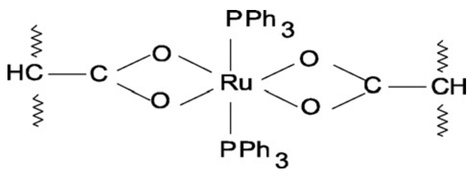
Fig. 4. IR spectra of the CCPAARu before and after reaction in epichlorohydrin.

CCPAARu (Fig. 3(a)) and used CCPAARu (Fig. 3(b)), showed that the recovered catalyst had a decrease of intensity of the band at 1632 cm^{-1} (monodentate) and an increase of the intensity of the band at 1566 cm^{-1} [υ_{as}(OCO) bidentate]. This effect may be ascribed to the free carboxylic groups present in the catalysts which coordinate to the metal with formation of metallic units bound to two carboxylate groups. Sbrana et al. [7] and Valentini et al. [8] reported that on reusing ruthenium complexes supported in linear PAA and alternate copolymers of maleic acid with vinyl monomers for hydrogenation and isomerisation of olefins, the activity of the catalysts dropped significantly. It was shown to arise from the formation of catalytically inactive bis-carboxylate species (Scheme 2). This latter problem can be prevented by neutralizing or esterifying the groups.

In the present study, the transfer hydrogenation of 2,6-dichlorobenzaldehyde was carried out in 5 ml of epichlorohydrin as the reaction medium using CCPAARu recovered after usage for the third time at 140 °C. The conversion of 2.6-dichlorobenzaldehyde to 2,6-dichlorobenzyl alcohol at 24 h is 100%. IR spectra of the CCPAARu catalyst before and after reaction in epichlorohydrin are shown in Fig. 4(a) and (b). It can be seen that the absorption band at 1632 cm^{-1} [υ_{as}(OCO) monodentate] increases after reaction in epichlorohydrin. This is because epichlorohydrin reacts with uncoordinated carboxylate groups to form ester structures and prevents the formation of catalytically inactive bis-carboxylate species. It also possibly converted the bis-carboxylate species to a monocarboxylate species.

It is well known that when multidentate groups (in general bidentate) coordinate to metals, the metal leaching can be reduced. In our case the small amount of metal leaching of the CCPAARu catalyst may be a result that more than one carboxylate groups is bound to the ruthenium centre.

Based on the above results, it can be proposed that formation of a non-hydrido species [2] during catalytic reaction is the main cause of the catalyst deactivation.



Scheme 2.

3.7. *Enhanced activity of the CCPAARu catalyst*

Although the local concentration of active metal centre in supported catalysts is higher than that for the homogeneous analog at the same level of catalyst used, due to the insolubility of polymer supports, the activities of polymer supported catalyst are not always higher than those of homogeneous analogs. This is because in polymer supported catalysts generally, only a fraction of the total metal units are involved in catalysis. To obtain more active polymer supported catalysts than homogeneous complexes, firstly, good swellability of the support is needed. Secondly, the substrates must easily diffuse into the active metal centre and cause the reaction to take place. Also, the reaction products must easily go into solution, making way for new portions of substrate. Therefore, a comparison of the activities of the CCPAARu to its small molecule precursor, $RuH_2(PPh_3)_4$, was carried out. The same amount of small molecule precursor as supported on the CCPAA absorbent was used to catalyze the transfer hydrogenation of 2,6-dichlorobenzaldehyde at the same reaction conditions. The results show that the conversion of 2,6-dichlorobenzaldehyde to 2,6-dichlorobenzyl alcohol is 58.4% catalyzed by the small molecule, but 90% conversion of 2,6-dichlorobenzaldehyde catalyzed by the CCPAARu was obtained. It suggests that using swellable supports and suitable liquid media can achieve higher active catalysts. Another reason of higher activity of the CCPAARu may be the presence of coordinative unsaturation. The presence of coordinative unsaturation has been demonstrated by Braca et al. [9] on the basis of ESR investigations. Braca et al. [10] reported that polycarboxylate bound Ru(II) complexes show higher activity than monomeric analogs, depending on swelling interactions between polymer ligand and liquid medium and on the presence of coordinatively unsaturated species. From this study, it shows that the CCPAARu has higher activity than the monomeric analog $RuH_2(PPh_3)_4$ and CCPAA absorbent.

3.8. *Reaction kinetics*

Fig. 5 shows the conversion of 2,6-dichlorobenzaldehyde to 2,6-dichlorobenzyl alcohol as a function of reaction time at a temperature of 140 °C. It suggests that it exhibits an apparently first-order dependence on the aldehyde concentration for most of the reaction. Good linear relationship is observed by logarithmic plots of ln[Aldehyde] vs. reaction time shown in Fig. 6. The values in Fig. 6 were obtained from the data points of conversion plot of Fig. 5 for more than 90% completion of the reaction. The slope of the logarithmic plots provides values of the pseudo-first-order

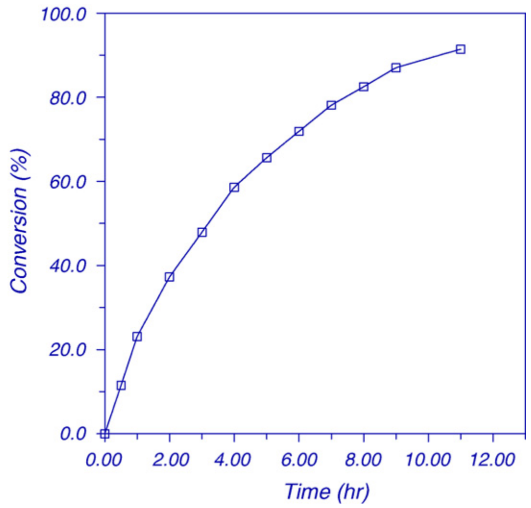


Fig. 5. Representative transfer hydrogenation plot for the hydrogenation of 2,6-dichlorobenzaldehyde.

rate constant k'. In Table 4 a summary of the results for a series of experiments showing the effect of reaction variables on k' is provided. Replicates of many experiments were carried out to study the reproducibility of the catalysis. The error in rate constants was found to be about ±5%.

3.9. *Effect of the amount of the catalyst*

The effect of total ruthenium amount on the initial rate of transfer hydrogenation was investigated. The source of ruthenium from the CCPAARu (1.86 Ru%) was presented in varying amounts ranging from 2.76×10^{-3} to 8.28×10^{-3} mmol. The experiments were carried out at concentrations of 0.13 M 2,6-dichlorobenzaldehyde and 0.52 mM cyclohexanol in 5 ml of 1,2-dichlorobenzene at 140 °C. The results are shown in Fig. 7 and indicate a linear dependence of the initial rate on catalyst amount ranging from 0.76×10^{-3} to 8.28×10^{-3} mmol.

In the control experiments without the CCPAARu catalyst, the results show that no transfer hydrogenation products were detected.

Table 4
Kinetic data for transfer hydrogenation of 2,6-dichloro-benzaldehyde from cyclohexanol[a].

Ru ($\times 10^3$ mmol)	[Alcohol] (M)	[Aldehyde] (M)	T (°C)	k' ($\times 10^3$ min^{-1})
6.44	0.52	0.13	110	0.27
6.44	0.52	0.13	120	0.40
6.44	0.52	0.13	130	0.81
6.44	0.52	0.13	140	2.08
6.44	0.52	0.13	150	3.62
6.44	0.13	0.13	140	0.35
6.44	0.26	0.13	140	0.80
6.44	0.26	0.13	140	0.72
6.44	0.39	0.13	140	1.36
6.44	0.52	0.13	140	2.08
2.76	0.52	0.13	140	0.64
4.60	0.52	0.13	140	1.19
6.44	0.52	0.13	140	2.08
6.44	0.52	0.13	140	2.36
8.28	0.52	0.13	140	2.53
6.44	0.39	0.13	140	1.36
6.44	0.39	0.26	140	0.54
6.44	0.39	0.26	140	0.51
6.44	0.39	0.39	140	0.28
6.44	0.39	0.39	140	0.29
6.44	0.39	0.52	140	0.18

[a] 1,2-Diclorobenzene as solvent.

3.10. *Effect of hydrogen donor concentration*

The effect of the hydrogen donor concentration on the initial rate of transfer hydrogenation was investigated. The hydrogen donor, cyclohexanol was presented in concentrations ranging from 0.13 to 0.52 mM. The reaction was carried out with an initial 2,6-dichlorobenzaldehyde concentration of 0.13 M in 5 ml of 1,2-dichlorobenzene at 140 °C. A catalyst amount of 6.44×10^{-3} mmol Ru of the CCPAARu was maintained for this series of runs. The results obtained are shown in Fig. 8. It is noted that the initial rate shows a first-order dependence on the concentration of cyclohexanol.

3.11. *Effect of temperature*

The effect of temperature on the reaction rate constant was observed from an Arrhenius plot. A number of kinetic runs were carried out at several temperatures ranging from 110 to 150 °C. The reaction was carried out in 5 ml of 1,2-dichlorobenzene using a total ruthenium amount of 6.44×10^{-3} mmol Ru of the CCPAARu, an initial 2,6-dichloro-benzaldehyde concentration of 0.13 M and a

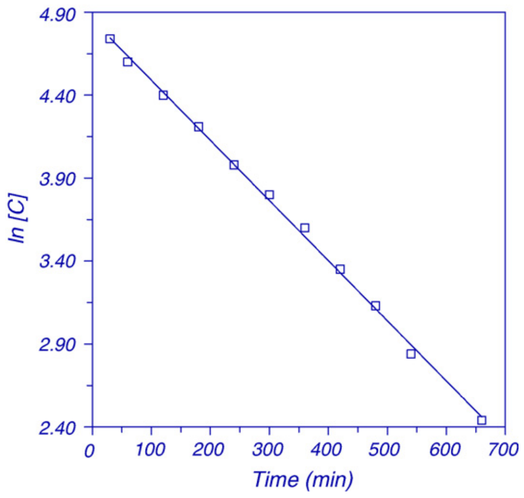


Fig. 6. Logarithmic lot of ln[Aldehyde] vs. time for the transfer hydrogenation of 2,6-dichlorobenzaldehyde.

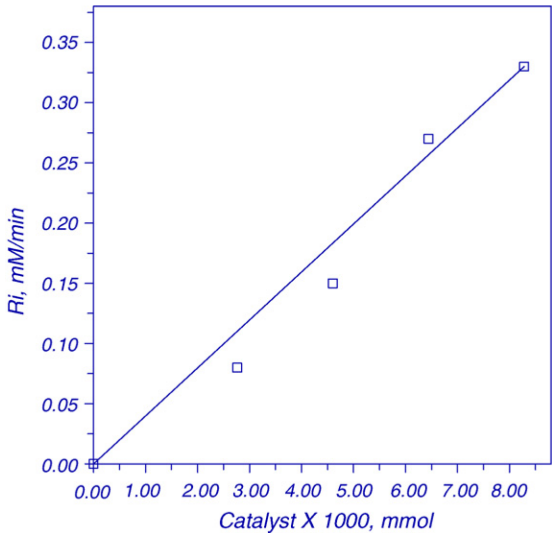


Fig. 7. Dependence of the initial rate on the catalyst amount.

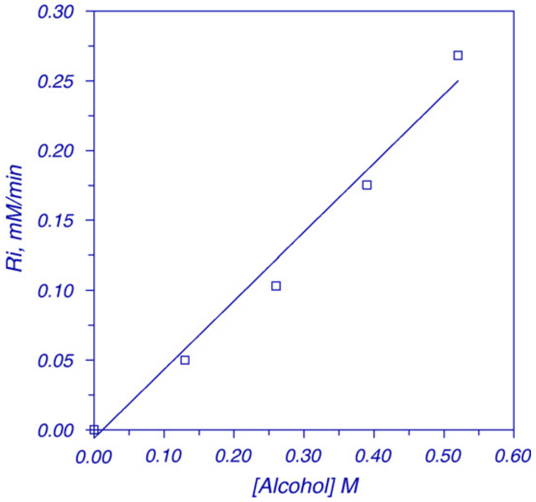


Fig. 8. Dependence of the initial rate on the concentration of hydrogen donor.

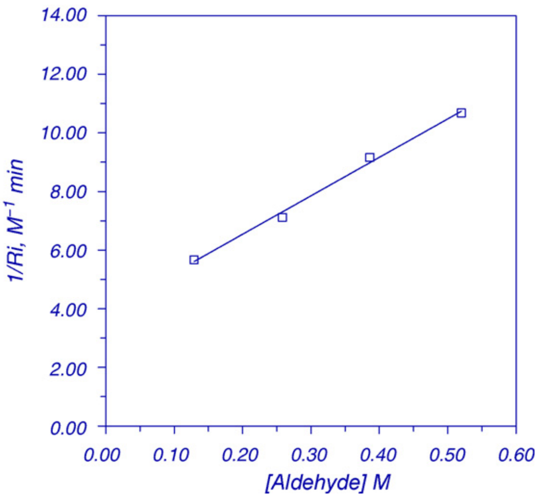


Fig. 10. Dependence of the initial rate on the concentration of aldehyde.

cyclohexanol concentration of 0.52 mM. Fig. 9 shows a good linear Arrhenius plot. From Fig. 9 the activation energy, Ea, 22 ± 1 kcal/mol was obtained, which is typical of a chemically controlled transfer hydrogenation reaction.

3.12. Effect of aldehyde concentration

The effect of aldehyde concentration was investigated. Hydrogen acceptor, 2,6-dichlorobenzaldehyde was present at concentrations ranging from 0.122 to 0.488 mM. The reaction was carried out at a concentration of 0.39 M cyclohexanol in 5 ml of 1,2-dichlorobenzene at 140 °C. A catalyst amount of 6.44×10^{-3} mmol Ru of the CCPAARu was maintained for this series of runs. The results shown in Fig. 10 indicate that the initial rate of the reaction decreased with an increase of aldehyde concentration. It is thought that the aldehyde has strong coordinating ability and that a considerable amount of two aldehyde molecules complexes (IV), as seen in Scheme 3, exists in the reaction system. Two aldehyde molecules complexes could not be reduced to corresponding alcohol because without coordination of hydrogen donors. Strong coordinating ability of aldehydes is confirmed by the observation that the reaction rate constant was not decreased by addition of triphenylphosphine, as discussed in the following section. The strong coordinating power of aldehydes was also reported by Imai studying the hydrogen transfer from organic compounds to aldehydes and ketones catalyzed by small molecule of $RuH_2(PPh_3)_4$ [5].

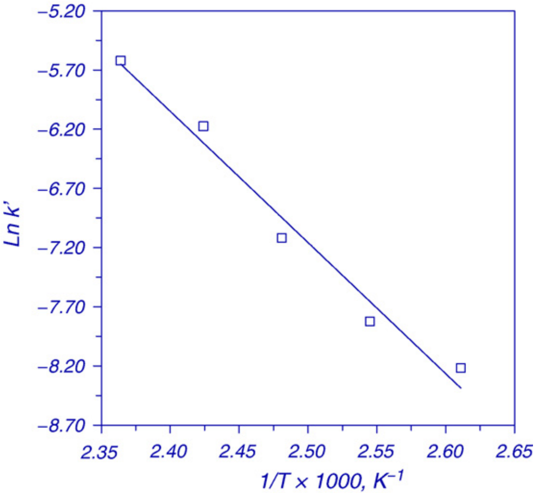


Fig. 9. Dependence of the rate constant on the temperature.

3.13. Effect of added triphenylphosphine

To further investigate the reaction process, the effect of added triphenylphosphine (PPh_3) was examined at 140 °C. It is indicated that the rate constant of hydrogen transfer reaction was not affected at all by the addition of the PPh_3 concentration range of 0.01–0.1 M. This observation suggests the coordinating power of the aldehydes is so strong as to replace the triphenylphosphine from P-$RuH(PPh_3)_3$ catalyst even in the presence of an excess of the phosphine. In other words, the release of the PPh_3 from catalyst occurs easily due to the strong complexing ability of the aldehydes. This result is in accordance with the study of aldehyde concentration effect.

3.14. Mechanistic considerations and rate law

Imai et al. studied the kinetics of small molecule of $RuH_2(PPh_3)_4$ catalyzed hydrogen transfer hydrogenations from organic compounds to aldehydes and proposed the reaction mechanism [5]. The rate law expression obtained from proposed mechanism was found to accommodate all of their experimental observations fairly well. They also reported the IR study result that spectrum at 1520 cm^{-1} was attributed to the coordinated aldehyde of carbonyl group.

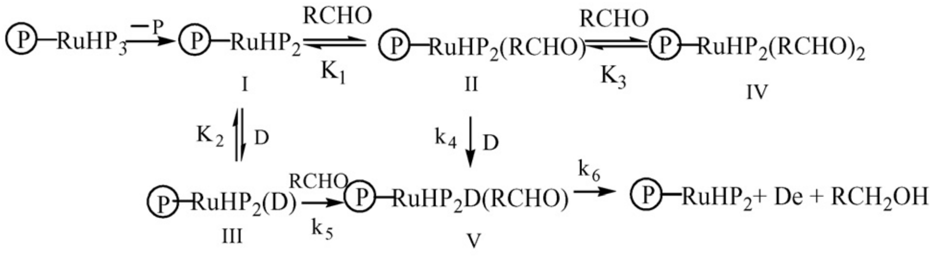
Based on the results described earlier and a comparison with the mechanism of the transfer hydrogenation from organic compounds to olefins, aldehydes and ketones catalyzed by small molecules of $RuH_2(PPh_3)_4$ and $RhCl(PPh_3)_3$ [11–15,5], Scheme 3 is reasonably proposed for the catalytic cycle of the hydrogen transfer reaction from cyclohexanol to the aromatic aldehydes catalyzed by the supported heterogeneous catalyst. Here, P-$RuHP_3$ stands for the CCPAARu catalyst.

Based on Scheme 3, it is reasonable to assume that intermediate V decomposes rapidly to the product and hence the following rate law can be expressed as Eq. (2):

$$R = k_4[\mathrm{II}][\mathrm{D}] + k_5[\mathrm{III}][\mathrm{RCHO}] \quad (2)$$

The total concentration of metal catalyst $[\mathrm{Cat}]_\mathrm{T}$ is given by Eq. (3):

$$[\mathrm{Cat}]_\mathrm{T} = [\mathrm{I}] + [\mathrm{II}] + [\mathrm{III}] + [\mathrm{IV}] \quad (3)$$



D = hydrogen donor, De = dehydrogenation product of donor, P = PPh$_3$.

Scheme 3.

The equilibrium constants, K_1, K_2, and K_3 are defined by Eqs. (4)–(6):

$$K_1 = \frac{[\mathrm{II}]}{[\mathrm{I}][\mathrm{RCHO}]} \tag{4}$$

$$K_2 = \frac{[\mathrm{III}]}{[\mathrm{I}][\mathrm{D}]} \tag{5}$$

$$K_3 = \frac{[\mathrm{IV}]}{[\mathrm{II}][\mathrm{RCHO}]} \tag{6}$$

Rearrangement of Eqs. (4)–(6), followed by substitution into Eq. (3) produced Eq. (7):

$$[\mathrm{II}] = \frac{K_1[\mathrm{RCHO}][\mathrm{Cat}]_\mathrm{T}}{1 + K_1[\mathrm{RCHO}] + K_1K_3[\mathrm{RCHO}]^2 + K_2[\mathrm{D}]} \tag{7}$$

Eq. (5) can be rearranged as follows:

$$[\mathrm{III}] = K_2[\mathrm{I}][\mathrm{D}] \tag{8}$$

Rearrangement of Eq. (4), followed by substitution into Eq. (8) produced Eq. (9):

$$[\mathrm{III}] = \frac{[\mathrm{II}]K_2[\mathrm{D}]}{K_1[\mathrm{RCHO}]} \tag{9}$$

By substituting Eq. (7) into Eq. (9), Eq. (10) is obtained:

$$[\mathrm{III}] = \frac{K_2[\mathrm{D}][\mathrm{Cat}]_\mathrm{T}}{1 + K_1[\mathrm{RCHO}] + K_1K_3[\mathrm{RCHO}]^2 + K_2[\mathrm{D}]} \tag{10}$$

Finally substitution of Eq. (7), and (10) into Eq. (2), gives the rate expression as Eq. (11):

$$R = \frac{(k_4K_1 + k_5K_2)[\mathrm{RCHO}][\mathrm{Cat}]_\mathrm{T}[\mathrm{D}]}{1 + K_1[\mathrm{RCHO}] + K_2[\mathrm{D}] + K_1K_3[\mathrm{RCHO}]^2} \tag{11}$$

where K_1, K_2, and K_3 are equilibrium constants, k_4 and k_5 are rate constants, and [D], [RCHO], and $[\mathrm{Cat}]_\mathrm{T}$ are the concentrations of the hydrogen donor, aldehyde, and added catalyst, respectively.

As the initial rate against aldehyde concentration exhibited an inverse linear relationship (Fig. 10), the following relation should be satisfied in the denominator of Eq. (11), $1 + K_2[\mathrm{D}] \ll K_1[\mathrm{RCHO}](1 + K_3[\mathrm{RCHO}])$, that is, $[\mathrm{I}] + [\mathrm{III}] \ll [\mathrm{II}] + [\mathrm{IV}]$. This relation requires that coordination power of aldehyde is strong, and this is supported by the observation that the reaction rate was not decreased by the addition of triphenylphosphine. Consequently, the rate expression can be reduced to

$$R = \frac{k'[\mathrm{D}][\mathrm{Cat}]_\mathrm{T}}{1 + K_3[\mathrm{RCHO}]} \tag{12}$$

where k' is the observed rate constant, $(k' = (k_5K_2 + k_4K_1)/K_1)$. This expression is found to accommodate all of the other experimental observations fairly well. For example, the rate equation implies a linear dependence on the initial concentration of catalyst, which is in full agreement with the experimental results (Fig. 7). It also explains the rate-aldehyde concentration profile shown in Fig. 10.

4. Conclusions

A swellable polymer supported Ru(II) complex (CCPAARu) can be efficiently used for catalyzing the reduction of aromatic aldehydes by cyclohexanol to alcohols. The process was shown to depend on the structure of aromatic aldehyde. Electron-withdrawing groups enhance hydrogen transfer hydrogenation, while electron-donating substituents have a negative effect on the reaction rate. 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 was 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.

A kinetic study has been carried out in 1,2-dichlorobenzene at 140 °C. The kinetics of the reaction were measured between 100 and 140 °C. The process was shown to depend on the concentrations of aldehyde and hydrogen donor, and on the amount of catalyst. An apparent activation energy, $\mathrm{Ea} = 22 \pm 1$ 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. The rate expression $R = K'[\mathrm{D}][\mathrm{Cat}]_\mathrm{T}/(1 + k_3[\mathrm{RCHO}])$ accommodates all of the experimental observations fairly well.

References

[1] C.U. Pitman, Jr., in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon press, Oxford, 1982, p. 533.
[2] Z.S. Liu, G.L. Rempel, J. Appl. Polym. Sci. 108 (2008) 3262.
[3] Z.S. Liu, G.L. Rempel, J. Mol. Catal. A Chem. 278 (2007) 228.
[4] Z.S. Liu, G.L. Rempel, J. Phys. Org. Chem. (submitted).
[5] H. Imai, T. Nishiguchi, K. Fukuzumi, J. Org. Chem. 41 (1976) 665.
[6] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Chem. Rev. 85 (1985) 129.
[7] G. Sbrana, G. Braca, G. Valentini, G. Pazienza, A. Altomare, J. Mol. Catal. 3 (1977) 111.
[8] G. Valentini, G. Sbrana, G. Braca, J. Mol. Catal. 11 (1981) 383.
[9] G. Braca, G. Sbrana, G. Valentini, A. Colligiani, C. Pinzino, J. Mol. Catal. 7 (1980) 457.
[10] G. Braca, F. Ciardelli, G. Sbrana, G. Valentini, Chim. Ind. (Milan) 59 (1977) 766.
[11] Y. Sasson, J. Blum, J. Org. Chem. 40 (1975) 1887.
[12] T. Nishiguchi, K. Fukuzumi, J. Am. Chem. Soc. 96 (1974) 1893.
[13] T. Nishiguchi, K. Tachi, K. Fukuzumi, J. Org. Chem. 40 (1975) 237.
[14] H. Imai, T. Nishiguchi, K. Fukuzumi, J. Org. Chem. 39 (1974) 1622.
[15] H. Imai, T. Nishiguchi, K. Fukuzumi, Bull. Chem. Soc. Jpn. 48 (1975) 1585.