ELSEVIER

Catalysis Today 66 (2001) 277–287

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Pt and Pt-alloy catalysts and their properties for the liquid-phase hydrogenation of cinnamaldehyde

Wanida Koo-amornpattana*, John Mike Winterbottom

School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

Abstract

The selective hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohol is not only of general interest in fine chemical and pharmaceutical intermediate production but also of specific relevance to the perfume and flavouring industries. A number of Pt/graphite catalysts have been prepared with metal loadings in the range 5–10 wt.% metal on graphite and with added cobalt in the composition range 5–99.5 mol%. These catalysts have been characterised using temperature programmed reduction (TPR) and have been compared with a commercial 5% (w/w) Pt/graphite catalyst for the hydrogenation of cinnamaldehyde in toluene and biphasic toluene/aqueous solutions containing a range of bases or potassium based salts. The reactions were carried out in a stirred reactor in the pressure range 4–11 bar absolute, in the temperature range 298–373 K, and with the concentration of cinnamaldehyde in the range 0.038–0.303 kmol/m^3. The presence of strong bases was found to enhance both catalyst activity and selectivity to cinnamyl alcohol. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Liquid-phase; Hydrogenation; Cinnamaldehyde; Pt catalyst

1. Introduction

The selective hydrogenation of an α,β-unsaturated aldehyde to its unsaturated alcohol, such as cinnamaldehyde to cinnamyl alcohol, is of importance in fine chemicals manufacture and particularly in respect of fragrances and flavourings.

The production of the unsaturated alcohol using homogeneous catalysts has been reported to be possible, with very high selectivity for a number of α,β-unsaturated aldehyde [2]. In the case of heterogeneous catalysts the attainment of high selectivity is more difficult and very dependent on the nature of the aldehyde and requires catalyst modification and promotion [3–7,15].

Pt–Co catalysts have been investigated and characterised by Moraweck et al. [1]. This study has focussed on graphite supported Pt and Pt–Co catalysts and the effects of the use of biphasic solvents and the presence of basic salts on activity and selectivity; the effects of basic media have been reported by Gallezot and Richard [13].

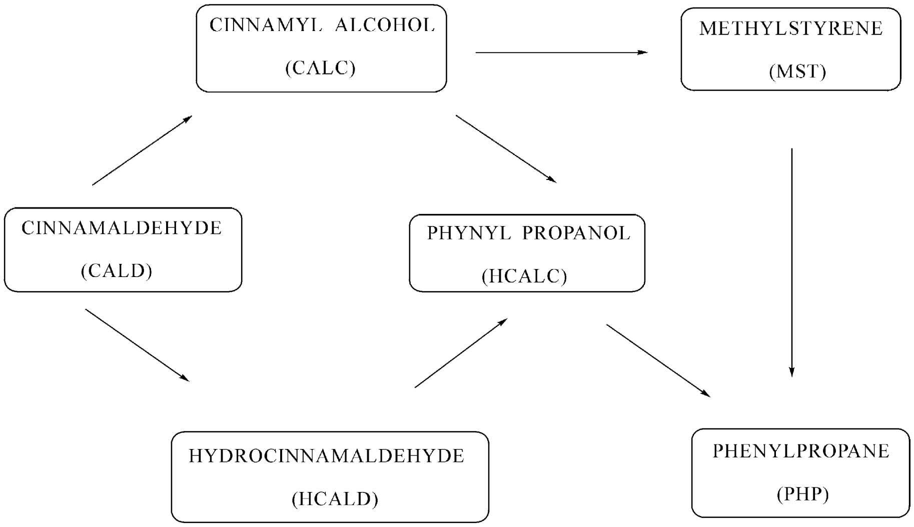
2. Catalytic reaction studies

Recently, the selective hydrogenation of cinnamaldehyde has been investigated in three phase systems [2–7,15]. The hydrogenation of cinnamaldehyde is shown in Scheme 1. Normally, during the reaction of cinnamaldehyde, both the carbonyl C=O group and the C=C double bond of cinnamaldehyde are hydrogenated and there are two parallel processes, from

---

* Corresponding author.
E-mail address: wxk664@hotmail.com (W. Koo-amornpattana).

PII: S0920-5861(00)00654-4



Scheme 1. (Reaction) Hydrogenation of cinnamaldehyde.

cinnamyl alcohol and hydrocinnamaldehyde, to form the final product (hydrocinnamyl alcohol). This reaction represents a characteristic problem and is typified by the selective hydrogenation of cinnamaldehyde, where there is a preference for one product (cinnamyl alcohol).

3. Experimental

Bimetallic catalysts were prepared in-house using a co-impregnation method. For characterisation, the bimetallic catalysts (Pt–Co) were studied by temperature programmed reduction (TPR). TPR peaks were measured at the temperature corresponding to the maximum hydrogen consumption rate and recorded at that temperature.

The hydrogenation of cinnamaldehyde was carried out in a stainless steel autoclave reactor of 1000 cm^3 capacity provided with a glandless magnetically-driven impeller, four baffles, gas inlet, sample port, vent, and external heating. The temperature in the autoclave was measured by a thermocouple. Hydrogen for the hydrogenation reaction was supplied by a hydrogen control unit (HCU).

The analysis of the cinnamaldehyde products and cinnamyl alcohol selectivity analysis was performed using gas chromatography (a PYE UNICAM series 304 with 3 m of an SP-1000 packed column with 0.625 cm i.d.).

4. Results and discussion

4.1. The characterisation of catalysts using TPR

TPR (Table 1) has been shown by Bosch et al. [8] to be a successful “fingerprint method” for the characterisation of reducible species. The TPR profile is characterised by hydrogen uptake for a wide temperature range. The reduction started at 450 K and was completed at 760 K.

As seen in Fig. 1, the TPR profiles indicated that alloying of some kind had occurred as there was a gradual increase in reduction temperature from 100 mol% Pt (503 K) to 100 mol% Co (760 K) and

Table 1
Operating conditions of TPR

Reducing gas	5% hydrogen/argon
Reducing gas flowrate (cm^3/min)	40–45
Temperature range (K)	293–1073
Heating rate (K/min)	12
Chart recorder sensitivity (typical) (mV)	5–100

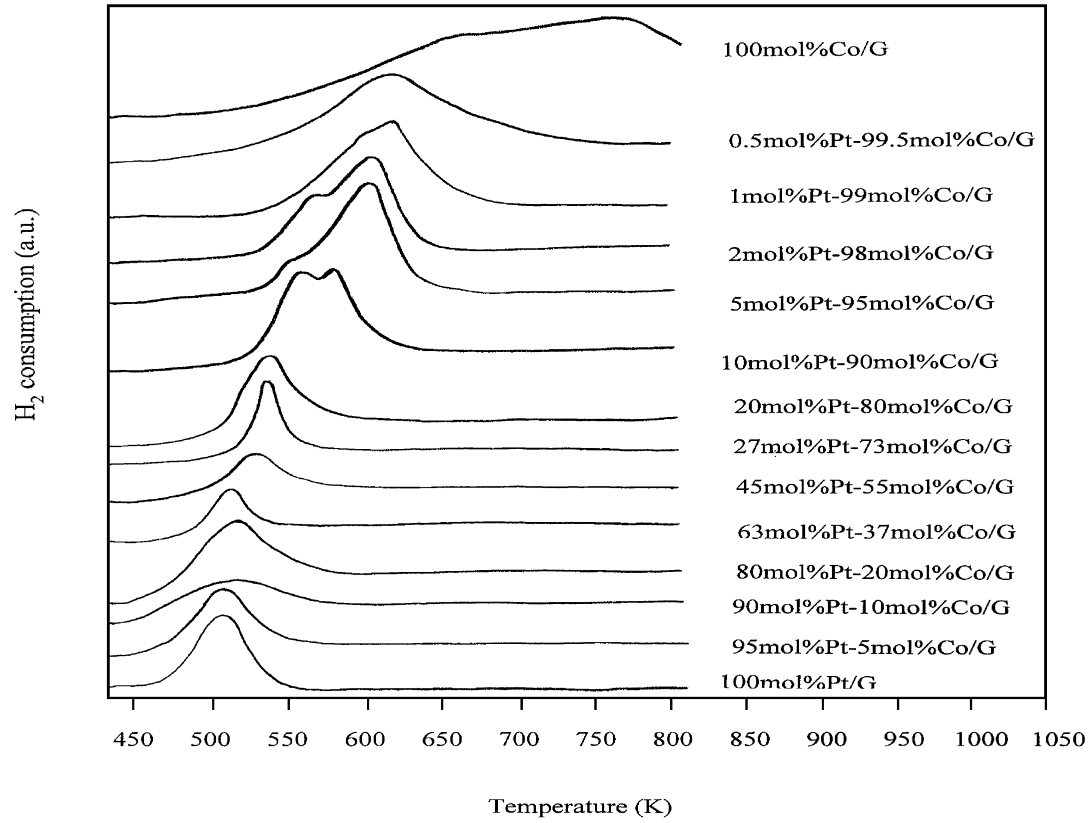


Fig. 1. The TPR profile of the various molar percentages of Pt–Co on graphite. Process conditions described in Table 1.

this result is in good agreement with Juszczyk et al. [9] and Van't Blik et al. [10]. The reduction peak for 100 mol% Co/G is very indistinct and may result from interaction with the support, although this is not expected to be strong. The presence of even a small quantity of Pt gives a much sharper reduction peak and a progressive decrease of reduction temperature suggests a synergistic effect of Pt with respect to Co.

4.2. Cinnamaldehyde hydrogenation

For the hydrogenation of cinnamaldehyde, both activity and selectivity were studied to assess those factors, which might lead to higher activity and improved selectivity to cinnamyl alcohol (Tables 2 and 3).

4.2.1. Bimetallic catalyst studies

A comparison of the activity and selectivity of bimetallic catalysts is shown in Fig. 2. As seen in Fig. 2(A), the catalyst activity for cinnamaldehyde hydrogenation as a function of alloy composition was a relatively complex function and for toluene as solvent showed maximum activity for the 100 mol% Pt catalyst with another lower maximum at about 50–60 mol% Co in Pt. When the solvent system was toluene/water (1:1), again 100 mol% Pt was of highest activity but alloys in the range 30–70 mol% Co in

Table 2
Process parameters employed using platinum catalysts for cinnamaldehyde hydrogenation

Catalyst	5 wt.% Pt/G
Catalyst loading (kg/m^3)	3.3–10
Substrate concentration (kmol/m^3)	0.038–0.303
Hydrogen partial pressure (bar absolute)	4–11.0
Temperature (K)	298–373
Reactor volume (m^3)	3×10^{-4}
Stirring speed (rpm)	1000

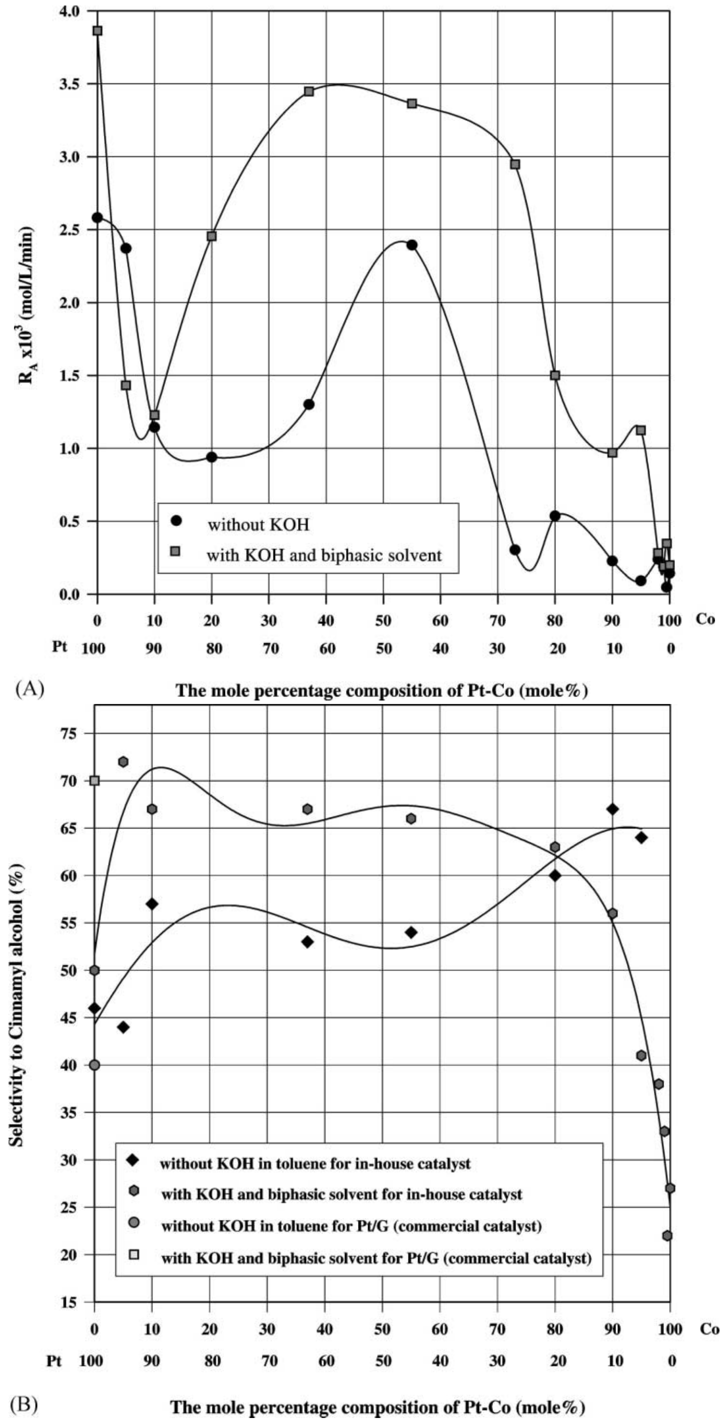


Fig. 2. (A) The catalyst activity of cinnamaldehyde hydrogenation in toluene and toluene/water with KOH at different molar percentage of Pt–Co on graphite at 298 K, 11 bar absolute, catalyst used 3.3 kg/m^3, cinnamaldehyde concentration 0.076 kmol/m^3, KOH concentration 0.077 mol/l. (B) The selectivity (at 30% cinnamaldehyde conversion) of cinnamaldehyde hydrogenation in toluene and toluene/water with KOH at different molar percentage of Pt–Co on graphite at 298 K, 11 bar absolute, catalyst used 3.3 kg/m^3, cinnamaldehyde concentration 0.076 kmol/m^3, KOH concentration 0.077 mol/l.

Table 3
Platinum catalyst promoter variables

Catalyst	5 wt.% Pt/G
Catalyst promoter	Co
Catalyst promoter loadings (mol%)	5–99.5
Promoter salts	KOH, CH_3COOK, KCl, NH_4OH, LiOH, NaOH, KNO_3
KOH (mol/l)	0.25–2.75
Promoter salts loadings (mol/l)	1.38

Pt gave a broad activity plateau and the activity was about 80% that of the 100 mol% Pt/graphite catalyst. However, the general pattern of behaviour is similar for both systems. However, a volcano type curve was not observed [12].

Promoting the platinum catalyst with increasing amounts of cobalt additive as shown in Fig. 2(B) further enhanced cinnamyl alcohol selectivity. Selectivity measurements showed that in a toluene solvent the highest selectivity to cinnamyl alcohol was exhibited by an "alloy" of composition 10 mol% Pt–90 mol% Co gave the selectivity 67%, while a biphasic toluene–water system containing potassium hydroxide gave optimum selectivity at 72% for an "alloy" of composition 95 mol% Pt–5 mol% Co. In the biphasic toluene/water system, the selectivity value for 100 mol% Pt/G is surprisingly low and the commercial 100 mol% Pt/G catalyst gave a selectivity of about 70%. The same commercial catalyst in toluene only gave a selectivity of 40% which is very similar to the in-house catalyst. The reason for this discrepancy is not understood, since the value results obtained were the results of more than one measurement. They result from differences in the chemistry of the catalyst production.

In Table 4, it is clearly shown that the biphasic solvent (toluene/water) with potassium hydroxide improved the selectivity at higher conversion for 0–55 mol% Co/G, but again the commercial 100 mol% Pt/G catalyst gave a significantly higher selectivity than that produced "in-house".

4.2.2. *Effect of various reaction parameters on activity and selectivity using a commercial Pt/G (Johnson Matthey Pt/G type 286) with a low area graphite*

4.2.2.1. Effect of temperature. From Fig. 3(A), the reaction rates increase with catalyst loading especially at lower temperatures [4]. However, the plot did not pass through the origin, and this may be caused by catalyst poisoning ($W_0 = 0.550\,\mathrm{kg/m^3}$). For catalyst loadings of $\leq 5\,\mathrm{kg/m^3}$, the rate is proportional to catalyst loading at all temperatures. The activation energy was found to be 3.7–4.8 kcal/mol.

Table 4
The selectivity of cinnamyl alcohol at different conversion of cinnamaldehyde using bimetallic catalysts in toluene and toluene/water

Catalysts	In toluene		In toluene/water[a]	
	Selectivity(%)	Conversion (%)	Selectivity(%)	Conversion(%)
100 mol% Pt/G (commercial)	43.6	40.1	81.5	68.9
100 mol% Pt/G	55.8	58.7	63.6	74.3
95 mol% Pt–5 mol% Co/G	45.2	17.9	74.8	75.1
90 mol% Pt–10 mol% Co/G	59.6	50.7	72.2	73.6
80 mol% Pt–20 mol% Co/G	45.9	51.5	68.7	54.2
63 mol% Pt–37 mol% Co/G	55.2	51.5	73.1	76.7
45 mol% Pt–55 mol% Co/G	65.0	76.9	74.3	82.1
27 mol% Pt–73 mol% Co/G	74.2	50.8	61.4	84.4
20 mol% Pt–80 mol% Co/G	65.5	35.7	66.2	68.8
10 mol% Pt–90 mol% Co/G	70.5	40.9	56.7	61.7
5 mol% Pt–95 mol% Co/G	64.6	33.4	45.8	62.7
2 mol% Pt–98 mol% Co/G	47.4	7.6	42.5	60.5
1 mol% Pt–99 mol% Co/G	49.6	9.1	40.3	43.0
0.5 mol% Pt–99.5 mol% Co/G	41.8	6.7	27.3	76.0
100 mol% Co/G	21.9	5.4	27.6	18.7

[a] The reaction taking place in toluene/water (1:1) with KOH = 0.077 mol/l as base.

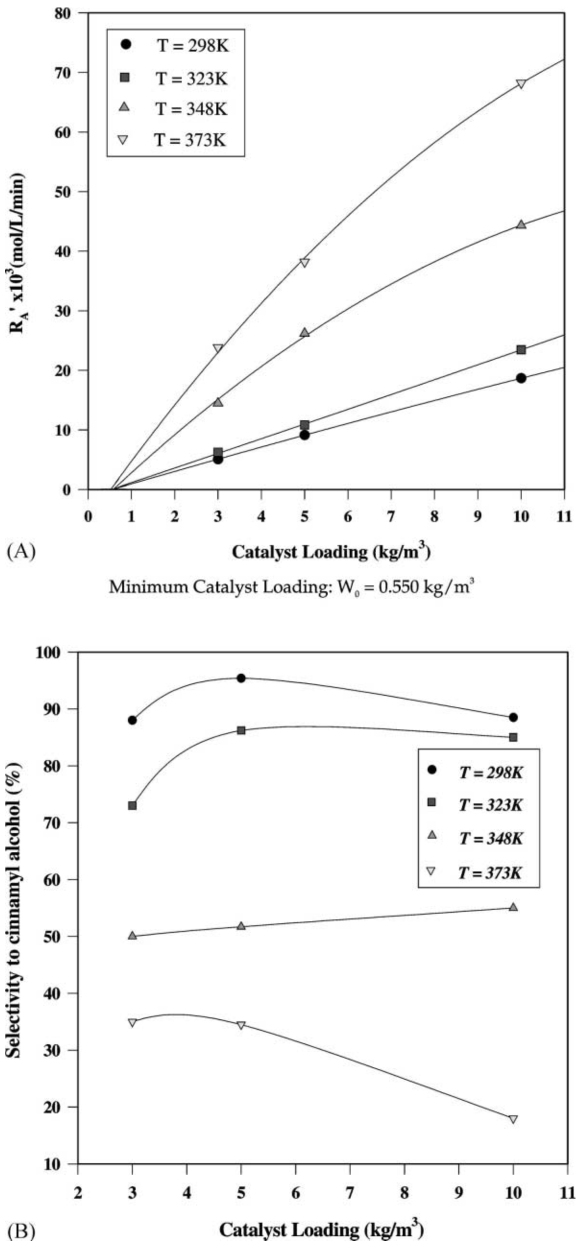


Fig. 3. (A) The catalyst activity for the cinnamaldehyde hydrogenation in toluene/water (1:1) with different temperature at various catalyst loadings. Process conditions described in Table 2. (B) The selectivity (at 90% conversion of cinnamaldehyde) of cinnamyl alcohol in toluene/water (1:1) with different temperature at various catalyst loadings. process conditions described in Table 2.

The cinnamyl alcohol selectivity is very temperature sensitive as demonstrated in Fig. 3(B), and it must be concluded that selectivity effects due to the influence of K^+ and/or OH^- are completely lost at high temperature and their interaction with the surface via adsorption will decrease as temperature increases.

4.2.2.2. Effect of hydrogen partial pressure. The order of the reaction with respect to hydrogen partial pressure was found by varying the partial pressure from 4 to 11 bar absolute. Fig. 4(A) demonstrates that the rate of reaction was of first-order in hydrogen partial pressure as has been reported by Satagopan and Chandalia [4] and Zhang et al. [7]. However, from Fig. 4(B), at 80% conversion there is no significant change of the selectivity to cinnamyl alcohol with the increase of hydrogen partial pressure.

4.2.2.3. Effect of cinnamaldehyde concentration. The kinetic data for the cinnamaldehyde hydrogenation over 5 wt.% Pt/G were obtained at different initial substrate concentration. From Fig. 5(A), the rate of reaction showed no significant change with increase in the concentration of cinnamaldehyde and the reaction was zero-order with respect to the concentration of cinnamaldehyde which agrees with previous results [4,7]. However, from Fig. 5(B), at 80% conversion the selectivity to cinnamyl alcohol increases with the concentration of cinnamaldehyde up to 0.227 kmol/m^3, after which it remains constant. It may well indicate that as base/cinnamaldehyde ratio increases for some reason the olefin group hydrogenation is enhanced.

A first-order reaction can be represented by the following expression [17]:

$$\frac{C^*_{\mathrm{H_2}}}{R_\mathrm{A}} = \frac{1}{k_\mathrm{L}a} + \frac{1}{w}\left(\frac{1}{k_\mathrm{s}a_\mathrm{c}} + \frac{1}{\eta k_\mathrm{r}a_\mathrm{c}}\right) \qquad (1)$$

where R_A is the reaction rate, $C^*_{\mathrm{H_2}}$ the equilibrium solubility of hydrogen, $k_\mathrm{L}a$ the volumetric mass transfer coefficient for gas absorption, w the catalyst loading, k_s the liquid–solid mass transfer coefficient, a_c the external particle area per unit mass, k_r the first-order rate constant, and η the effective mass factor, assumed to be one for a low area graphite.

Analysis of the results in Fig. 3(A) according to the above equation employed the Frössling equation in the

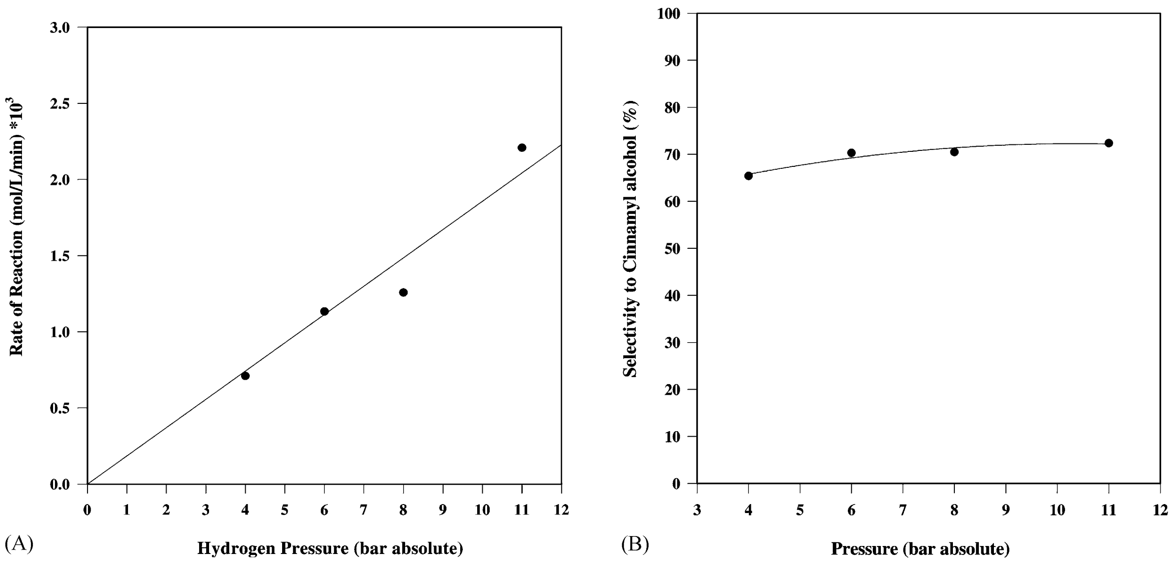


Fig. 4. (A) The catalyst activity of cinnamaldehyde hydrogenation in toluene/water (1:1) with various pressure. process conditions described in Table 2. (B) The selectivity (at 80% conversion of cinnamaldehyde) of cinnamyl alcohol in toluene/water (1:1) with various pressure. Process conditions described in Table 2.

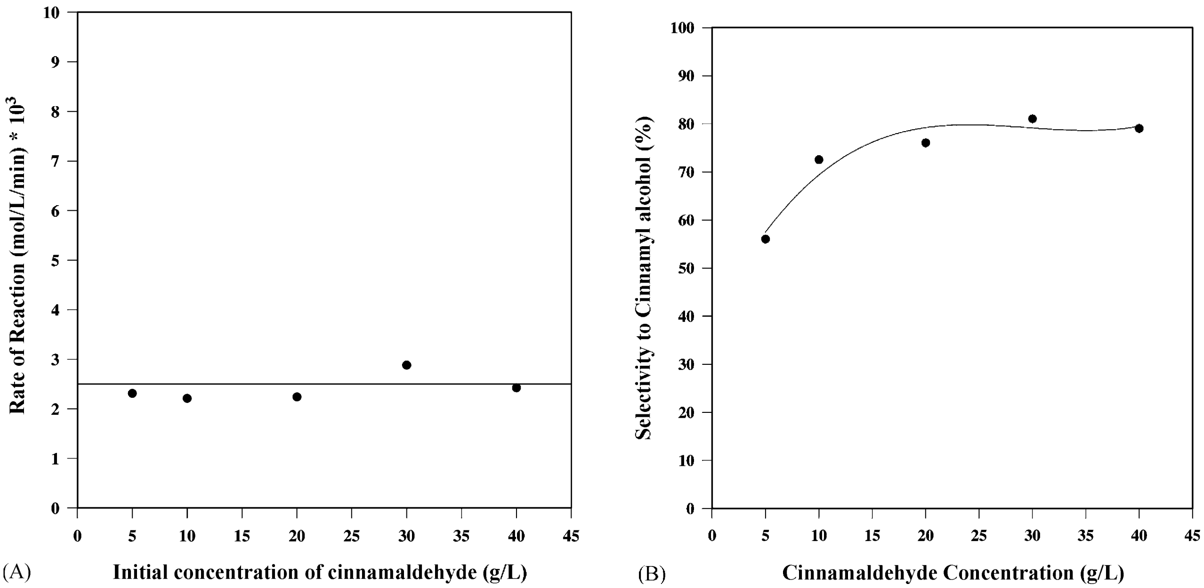


Fig. 5. (A) The catalyst activity of cinnamaldehyde hydrogenation in toluene/water (1:1) with different concentration of cinnamaldehyde. Process conditions described in Table 2. (B) The selectivity (at 80% conversion of cinnamaldehyde) of cinnamyl alcohol in toluene/water (1:1) with different concentration of cinnamaldehyde. Process conditions described in Table 2.

form

$$Sh = \frac{k_s d_p}{D_{AB}} = 2 + 0.6 Re_p^{1/2} Sc^{1/3} \quad (2)$$

where Sh is the Sherwood number, d_p the particle diameter, D_{AB} the diffusivity of H_2 in solvent, Re_p the particle Reynolds number, and Sc the Schmidt number.

This revealed that k_s was at least 1 order of magnitude larger than k_r. Hence, liquid–solid transport resistance was very low compared with reaction resistance. However, the contribution of $1/k_La$, obtained from the intercept of the $C^*_{H_2}/R_A$ vs. $1/w$ plot was found to be significant contributing 10–60% of the resistance and helps to explain why the apparent energy of activation is relatively low (3–5 kcal/mol); it would be expected to be >10 kcal/mol for surface reaction rate control. Gas absorption resistance may be significant due to the use of a biphasic solvent system such as toluene/water, which could inhibit transfer of hydrogen from gas to liquid phase.

4.2.3. Effects of basic and other potassium salts

A commercial 5% (w/w) Pt/G catalyst when employed with a toluene/water solvent containing KOH gave improved activity and selectivity. Fig. 6(A) shows that there is a linear increase over a range of 0.4–2.8 mol/l KOH, i.e. a first-order effect. It is also clear from Table 5 that the nature of the metal cation is of importance but when the associated ion is strongly basic the effect is greater. It has been reported [13] that an electropositive metal (with respect to Pt) can activate the C=O group as shown in Fig. 7.

The effect lies in the order $Li^+ > Na^+ > K^+$ and the charge density will lie in the same order. Other metal ions Fe^{2+} and Co^{2+} have given similar effects and the metal cation is thought to act as a Lewis acid with the lone pair on the oxygen. However, from Fig. 8, other weakly or non-basic potassium

Table 5
The activity of the reaction at various bases in toluene/water (1:1)

Promoter salts	Rate of reaction × 10^3 (mol/l/min)
LiOH	12.58
NaOH	9.48
KOH	7.56
KCl	3.98
CH_3COOK	3.86
KNO_3	2.55
NH_4OH	2.44

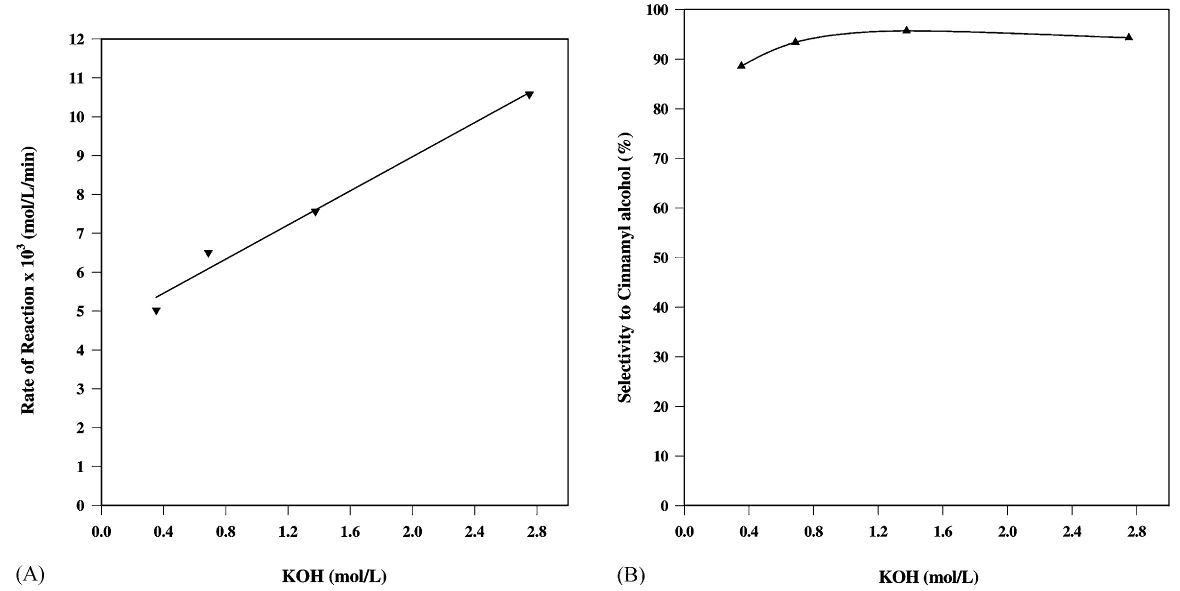


Fig. 6. (A) The catalyst activity of cinnamaldehyde hydrogenation in toluene/water (1:1) with various KOH at 298 K, 11 bar absolute, catalyst used 5 kg/m^3, cinnamaldehyde concentration 0.227 kmol/m^3. (B) The selectivity (at 85% conversion of cinnamaldehyde) of cinnamyl alcohol in toluene/water (1:1) with various KOH at 298 K, 11 bar absolute, catalyst used 5 kg/m^3, cinnamaldehyde concentration 0.227 kmol/m^3.

salts have no or only a small effect. Hence, the OH^- must play some part and has been observed to enhance the rate of crotonaldehyde hydrogenation except that *n*-butyraldehyde was produced not crotyl alcohol. Shama [16] proposed that OH^- protected the C=O group as shown in Fig. 9.

Cinnamaldehyde behaves very differently, but it may be that the greater steric effect of the benzene ring, in addition to its greater electron density combine to promote C=O bond hydrogenation. However,

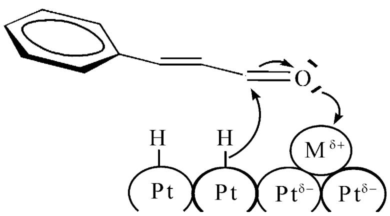


Fig. 7. The C=O group adsorbs via donation of a lone pair of electrons from the oxygen atom ($M^+ = Li^+$, Na^+, or K^+).

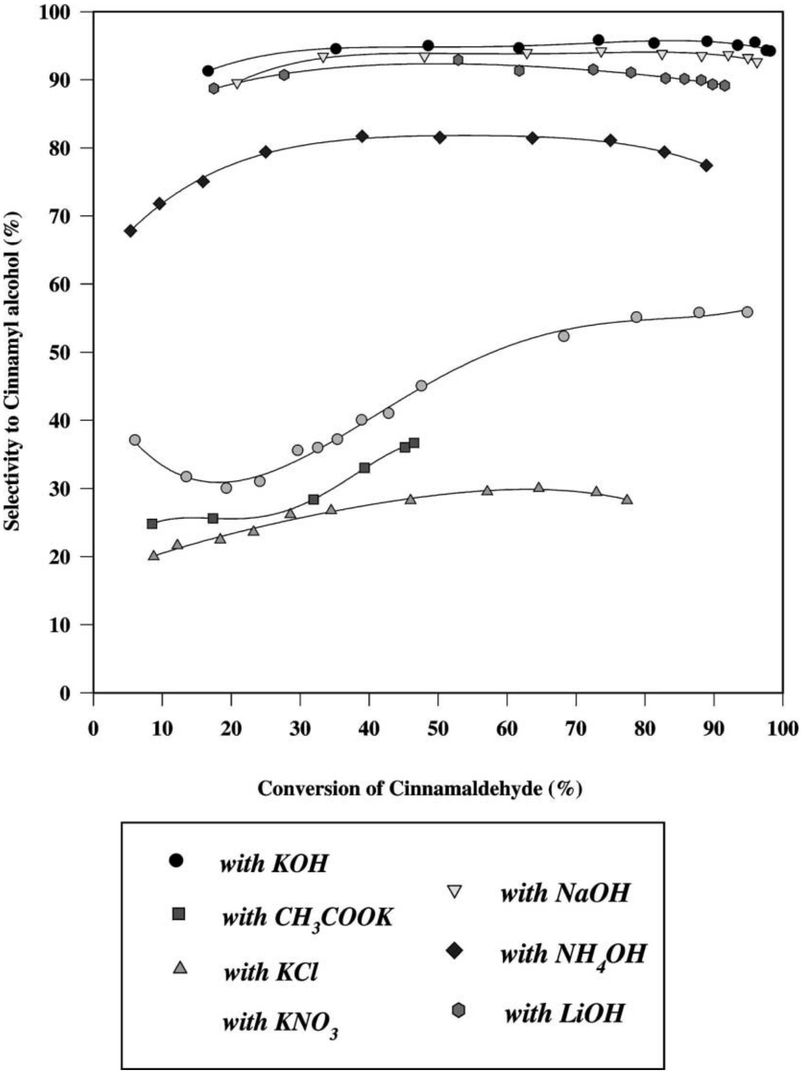


Fig. 8. The selectivity of cinnamyl alcohol in toluene/water (1:1) with different promoter salts concentration at 1.38 mol/l, 298 K, 11 bar absolute, catalyst used $5\,kg/m^3$, cinnamaldehyde concentration $0.227\,kmol/m^3$.

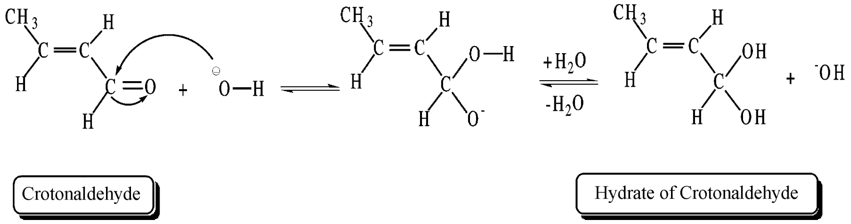


Fig. 9. Reaction mechanism for the formation of the hydrate of crotonaldehyde catalysed in the presence of a base [16].

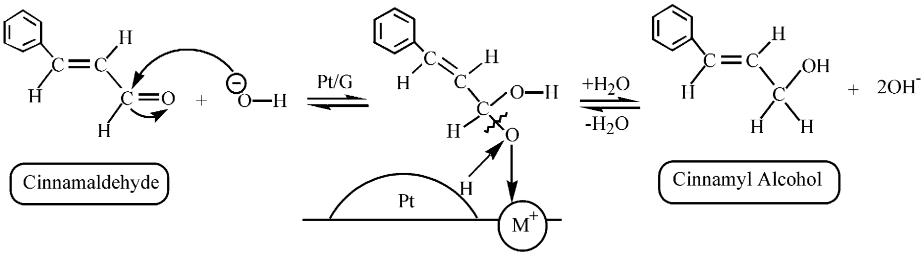


Fig. 10. Possible reaction mechanism for the formation of the cinnamyl alcohol catalysed in the presence of a base (M^+ is K^+, Na^+, or Li^+) [15].

there is a possibility that the OH^- ion combines in some way with the C=C bond, inhibiting its hydrogenation. The possible reaction mechanism in the presence of base can be shown in Fig. 10.

This assumption can be explained that for LiOH, NaOH, and KOH gave the excellent activity and selectivity in consideration of OH^- reacted with carbonyl group and made the donated of a lone pair of electrons from the oxygen atom ($M^+ = Li^+$, Na^+, or K^+). In addition, the lone pair electron from the oxygen atom interacted with H^+ and might be dissociated the remote C–O bond by M^+ ions. Moreover, due to the nature of the metal cation is of importance but when the associated ion is strongly basic the effect is greater [15].

The possible of using a weak base (NH_4OH) or the potassium salts (KNO_3, CH_3COOK, KCl) instead of alkali hydroxide was also investigated and it was found that the utilisation of these potassium salts or a weak base resulted in a drop in the reaction rate.

This is a speculative suggestion and would benefit from the use of D_2O or KOD to see where exchange occurred. It has been stated that base can give faster dissociation of catalyst-product complexes in homogeneous chiral reaction [14], but it is not possible to be more specific in this case without further detailed study. However, while the literature reports effects due to the metal ion (Fig. 7), there is little explanation as yet of the role of the OH^- ion, which is important as M^+ alone in the form of alkali metal ions is not effective in respect of rate and selectivity enhancement. Clearly, there is a co-promotional effect of M^+ and OH^-.

4.2.3.1. The variation of promoter salts. From Table 5, the rate of the reaction depends on the type of metal salts in the order LiOH > NaOH > KOH > CH_3COOK=KCl=KNO_3 > NH_4OH. LiOH gave the highest activity in the reaction.

5. Conclusions

1. The TPR profiles indicated that there is genuine interaction between the platinum and the cobalt.
2. The effects of promoting the 5% (w/w) Pt/G with Co on catalyst activity and selectivity were relatively complex and when the solvent system was toluene/water (1:1) with KOH, the activity was improved from 1.3×10^{-3} to 3.4×10^{-3} mol/l min at the similar conversion level and the selectivity

to cinnamyl alcohol was increased between 0 and 60 mol% Co from 44 to 73% at similar conversion level in a biphasic toluene–water system.

3. Promotion of platinum catalysts with bases enhanced selectivity to cinnamyl alcohol up to 96% at high conversion. Moreover, the selectivity to cinnamyl alcohol is strongly influenced by the OH^- group as shown in the order of $KOH > NaOH > LiOH > NH_4OH > KNO_3 > CH_3COOK > KCl$, but the metal cation is also influential and both M^+ and OH^- appear to be vital to high activity and selectivity.
4. The activity was increased by increasing the concentration of KOH, catalyst loading, and hydrogen partial pressure, but was constant with cinnamaldehyde concentration.
5. The selectivity decreased with increasing the temperature at similar conversion levels. In contrast, the selectivity improved with increasing concentration of cinnamaldehyde with no significant change when the hydrogen partial pressure was increased.
6. The reaction order is zero-order in cinnamaldehyde concentration and first-order in hydrogen partial pressure.
7. Activation energy measurements indicate that the reaction is significantly transport controlled and that gas absorption resistance is more significant than liquid–solid mass transport in its influence on energy of activation.

For further reading see [11].

Acknowledgements

The authors wish to thank Johnson Matthey (UK) for loan of the precious metal catalysts and salts. Thai Royal Government for financial support.

References

[1] B. Moraweck, R. Fréty, G. Pecchi, M. Morale, P. Reyes, Characterization and catalytic activity of Al_2O_3-supported Pt–Co catalysts, Catal. Lett. 43 (1997) 85–89.

[2] W. Yu, Y. Wang, H. Liu, W. Zheng, Preparation and characterization of polymer-protected Pt/Co bimetallic colloids and their catalytic properties in the selective hydrogenation of cinnamaldehyde, J. Mol. Catal. A 112 (1996) 105–113.

[3] S. Sharma, W. Koo-amornpattana, L. Zhang, S. Raymahasay, J.M. Winterbottom, in: F.F. Herkes (Ed.), Selective Hydrogenation of α,β-Unsaturated Aldehydes Using Pt and Ru Catalysts in Three Phase Reactors, Catalysis of Organic Reactions, Marcel Dekker, New York, 1998, pp. 583–590.

[4] V. Satagopan, S.B. Chandalia, Selective aspects in the multi-phase hydrogenation of α,β-unsaturated aldehydes over supported Noble metal catalysis, Part II, J. Chem. Technol. Biotechnol. 60 (1994) 17–21.

[5] Y.Z. Chen, S.W. Wei, Effect of promoter on selective hydrogenation of α,β-unsaturated aldehydes over cobalt borides, Appl. Catal. A 99 (1993) 85–96.

[6] T. Muroi, 1991. Advances in Precious Metal Catalyzed Processes, Chemical Catalysis News, Engelhard Corporation, UK.

[7] L. Zhang, J.M. Winterbottom, A.P. Boyes, S. Raymahasay, Studies on the hydrogenation of cinnamaldehyde over Pd/C catalysts, J. Chem. Technol. Biotechnol. 72 (1998) 264–272.

[8] H. Bosch, B.J. Kip, J.G.V. Ommen, P.J. Gellings, Factors influencing the temperature-programmed reduction profiles of vanadium pentoxide, J. Chem. Soc., Faraday Trans. 80 (1) (1984) 2479–2488.

[9] W. Juszczyk, Z. Karpinski, D. Lomot, J. Pielaszek, Z. Paal, A.Y. Stakheev, The structure and activity of silica-supported palladium–cobalt alloys, J. Catal. 142 (1993) 617–629.

[10] H.F.J. Van't Blik, D.C. Koningsberger, R. Prins, Characterization of supported cobalt and cobalt–rhodium catalysts, J. Catal. 97 (1986) 210–218.

[11] H.F.J. Van't Blik, R. Prins, Characterization of supported cobalt and cobalt–rhodium catalysts, J. Catal. 97 (1986) 188–199.

[12] D. Goupil, P. Fouilloux, R. Maurel, React. Kinet. Catal. Lett. 35 (1987) 185.

[13] P. Gallezot, D. Richard, Selective hydrogenation of α,β-unsaturated aldehydes, Catal. Rev.-Sci. Eng. 40 (1998) 81–126.

[14] M.V. Erasmus, H. Gröger, M. Shibasaki, Towards perfect asymmetric catalysis: additives and cocatalysts, Angew. Chem. Int. Ed. 38 (1999) 1570–1577.

[15] W. Koo-amornpattana, Ph.D. Thesis, University of Birmingham, UK, 2000.

[16] S. Shama, 1999. Ph.D. Thesis, University of Birmingham, UK.

[17] H.S. Fogler, Elements of Chemical Reaction Engineering, Prentice-Hall, Englewood Cliffs, NJ, 1986, pp. 596–628 (Chapter 12).