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The Effect of Different Coverage's of Bismuth on a 5% Pt/G Supported Catalysts on Enantiomeric Excess (*ee*) and Reaction Rate of Ethyl Pyruvate Hydrogenation Rate in Dichloromethane

Salem El Khaseh[1], Mohammed M .Bukhari[2], Salah Eldeen F. Hegazi[3]

[1]Head Group supervisor at sirte Oil Company Libya Assistant lecture at University of Benghazi, Libya

[2]Department of Chemical Engineering, Faculty of Engineering, University of Elimam Elmahadi , Kosti ,Sudan

[3]Department of Chemical Engineering, Faculty of Engineering, Jazan University , Saudi Arabia

Abstract: ***The primary objective of this study was to investigate the effect of reaction conditions, solvents, thermal annealing, the presence of CD-derivative and CN-derivative and sintering on the enantioselective hydrogenation of ethyl pyruvate, both distilled and non-distilled. In this work an autoclave reactor was used to carry out the reactions. The effect of pre-heating the Pt/graphite in 5% H_2/Ar at 700K was also investigated Also, the effect of bismuth adsorption on the catalyst for title reaction, in particular, the selective blocking of steps and chiral sites by (Bi) by G.A. Attardet al (1999), and its effect on enantioselectivity was to be investigated in order to augment previous work by Albdulrahmanet al (2005).Cyclic voltammetry (CV) is a widely used technique and can give much information concerning the coverage and structure of a metal electrode, in particular has allowed for detailed scrutiny of catalyst adsorption sites giving rise to enantioselectivity and therefore, new insights into structure-selectivity relationships. It has been used to investigate metal deposition and to characterise the morphology of catalysts under investigation, and also to assess the effects of catalyst modification by ad-atom adsorption and thermal annealing. In addition, investigate (i) the surface morphology of Pt particles of the terraces, steps and kinks present in as-received and conditioned catalysts and (ii) the adsorption of bismuth at Pt surfaces. By the selective blocking of Pt adsorption sites using bismuth ad atoms it is shown that the modifiers hydroquinine 4-chlorobenzoate (CD-der) and hydroquinidine 4-chlorobenzoate (CN-der) give rise to novel catalytic behaviour in relation to the enantioselective hydrogenation of ethyl pyruvate. It is reported that hydrogenation of ethyl pyruvate affords an enantiomeric excess(ee) to R-(S-) ethyl lactate in DCM if CD-der (CN-der) is adsorbed at step/defect sites whereas an excess of S- (R-) ethyl lactate results from adsorption of CD-der (CN-der) at Pt{111} terrace sites. Modified Pt catalysts supported on graphite (C) was investigated in order to determine the part played by the support in the reaction mechanism and then analyse enantioselectivities by using gas chiral chromatography (GC).***

Keywords: Enantioselective, heterogeneous, enantioselective, ethyl pyruvate

1. Introduction

In the last decades, homogeneous enantioselective catalysis has made phenomenal progress. Many transition metal complexes with chiral lingands have been developed for various catalytic reactions, important in the synthesis of optically pure compounds, in the fine chemicals and in pharmaceutical sectors. In terms, of Enantioselective hydrogenation of ketoesters using platinum in the presence of a modifier such as the cinchona alkaloid is a significant topic of current chemical research [1]. In fact, it has been recently reported that the high enantioselectivities of up to 95% can be observed for hydrogenation of α-ketoesters to the corresponding α-hydroxy esters for the optimised catalytic process (substrate, catalyst, modifier, solvent, and reaction conditions). In terms of asymmetric hydrogenation of α-ketoesters over cinchona alkaloid, Orito and co-workers [2] have reported first cinchona modified platinum and this is still a very significant research area [3]. Regarding, enantiomeric excess vital and excellent results up to 97% have been obtained in the reduction of ethyl pyruvate under optimum reaction conditions withthese Pt/ cinchona systems [4]. Although, the parts of the cinchonidine (CD) and cinchonine (CN) that give rise to activity are broadly understood however, we do not understand details [5]. Recent results of the enantioselective hydrogenation of ethyl pyruvate over Pt/C and Pt/Al_2O_3 catalysts modified with cinchonidine (CD ≥ 97%) and cinchonine (CN ≥99%) were obtained. It has been found that Pt/C modified cinchonidine enhance the reaction rate. However, when Bismuth (Bi) was deposed on Pt/C, a rate enhancement was observed and *ee* is decreased. In addition, the effect of thermal annealing and sintering on the enantioselective hydrogenation has been studied. Therefore, the best value of the R- enantiomeric excess (*ee*) was 57% for Pt/C that annealed at 700º K with high conversion. An *ee* of 74% and up to 100% conversion were obtained for CD-modified 5% Pt/Alumina in DCM as expected based on previous work by [6]. In the present study we have tried to investigate and to assess the effect of bismuth adsorption on the title reaction, and in particular to determine whether selective blocking of steps and chiral kink sites [7]. As found previously in the literature, the expected enantioselective outcome was very different in that, using DCM as a solvent, the CD-der gave a much lower *ee*(R) than CD and in fact the CN-der (epimer) gave a higher *ee*(R) than CD-der. That is there was an inversion of the selectivity expected using pure CD or pure CN. Surprisingly, the only (S) outcome was observed using the CD-der *in* DCM with increasing dosing volume of bismuth. The CN-der also was found to give the “expected” outcome in that it favoured a moderate *ee* of ~ 30% (R). So what is happening? Hutchings *et al* [8] have suggested that there is a change in the conformation of the CD-der and CN-der both as a function of modifier solution concentration and pH. The change in the conformation of the chiral auxiliary is then thought to reflect a change in *ee.* Clearly, in the present context, this offers a simple explanation of previous findings in that CD and CN are being generated in situ from CD-der and CN-der such that, if the CD-der is in competition with CD for adsorption sites then clearly this will result in an apparent change in the sign of *ee*. This study describes a complete set of enantioselective hydrogenation data for fully reduced graphite support in order to complete the present study (see last paper) into the role of the support in the Orito reaction. It is an interesting thought that the relative acidities of different supporting materials may play a decisive role in the surface chemistry.

The objective of this investigation was mainly to study the effect of CD-modified bimetallic catalysts on enantioselectivity and reaction rate of ethyl pyruvate hydrogenation. This was achieved via the following benchmarks:

1. An investigation of the effect of different coverages of bismuth on a 5% Pt/G supported catalysts on enantiomeric excess(*ee*) and reaction rate.
2. Detailed studies of the effect of thermally annealing Pt/G catalysts and subsequent deposition of Bi to form Bi-modified annealed catalyst in relation to the enantioselective hydrogenation of ethyl pyruvate was also to be carried out.
3. To investigate the effect of catalyst support on rate of the enantioselective hydrogenation of ethyl pyruvate over (*CD*-derivative) and (*CN*-derivative) modified platinum graphite
4. To use cyclic voltammetry as a probe to study the catalyst surface morphology.
5. To investigate the effect of adsorption at step/kink and terrace sites on the catalyst performance in enantioselective reactions.
6. To investigate the influence of solvent on the rate the enantioselective hydrogenation.

2. Material and Methods

2.1 Materials

2.1.1. Catalysts

In the present study, one type of supported catalyst was used both as received and after treatment at 700K in hydrogen from Engelhard (E 4759). Platinum/graphite (Pt/G; 5%) was obtained from Johnson Matthey having a low surface area of 2.1 $m^2 g^{-1}$ with a mean platinum particle diameter of 14 nm .The physical properties of this catalyst are reported to be as follows: Pt-content, 5% (w/w); Pt dispersion, 22%; mean Pt particle size, 4.5 nm [9].

2.1.2 Reactants and reagents

Ethyl pyruvate (*etpy*≥ 97% purity) was obtained from Fluka. Modifiers such as hydroquinine 4-chlorobenzoate and hydroquinidine 4-chlorobenzoate (Figure 1) were obtained from Aldrich Chemicals and used without further purification. In this study, cinchonidine is mainly used for enantioselective hydrogenation (from henceforth, this reactant will be referred to as *CD;* 98% purity). Cinchonine, (from henceforth, this reactant will be referred to as *CN;* 98% purity) the near enantiomer of cinchonidine was used for a few experiments. Dichloromethane (DCM HPLC grade, 12.5 ml) as received from Fisher Scientific was mixed with *etpy* and treated with acetic acid (2.5 ml) as solvent in addition, the purity of hydrogen is 99.99% as received from BOC Gases.

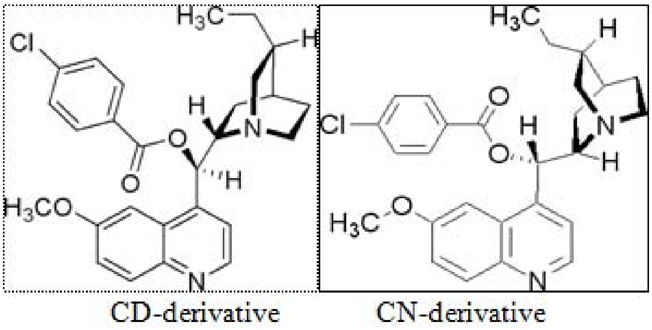

Figure 1: Structures of hydroquinine 4-chlorobenzoate (CD-derivative) and hydroquinidine 4-chlorobenzoate (CN-derivative).

2.2 Addition of bismuth Bi $(NO_3)_3$ to platinum surface

2g samples of Platinum/graphite (Pt/C), were used as received. Fully reduced graphite supports were placed in a 100 ml evaporating basin with a magnetic stirrer bar. A solution of 3.63 x 10^{-4} M was prepared by addition of $Bi(NO_3)_3$ (35.9 mg, 0.0359g; 98+%; A.C.S. reagent, Aldrich) in 250 ml of ultra-pure water, in a flat bottom flask. Then it was stirred for 4 h. The slurry was then filtered off under vacuum and washed with 200 ml of ultra-pure water three times to remove any remaining nitrate. Finally, the catalyst was dried under vacuum at room temperature overnight and used immediately [10].

3. Procedure

All reactants were immediately measured into the glass liner and placed in the sealed autoclave. The autoclave was purged three times with hydrogen to a pressure of 4 bar to remove air. After purging, the vessel was pressurised with hydrogen to 35 bar, the reaction was then started by stirring 1500 rpm to start the reaction and the reaction was then stopped by stopping the stirring and decreasing the hydrogen pressure. Then its product was isolated and analysed by using chiral GC. In addition, the rate of reaction was monitored by determining the hydrogen uptake every 10 s with each reading being relayed to a computer and stored Mevellec et al 2004 [2]. Cyclic voltammetry (CV) was used to study the catalyst surface of Pt/G and to study an electrochemical system by sweeping the potential of working electrode from E_1(initial value) to a potential E_2. Then the direction of sweep is reversed and the electrode potential scanned back to E_1 whilst monitoring continuously the flow of electric current in the cell. It has been found that filled the defect sites on Pt/G surface and thermal annealing and sintering was investigated by CV as well.

4. Calculation of Adsorbate Coverage

4.1 Adsorbate coverage of Bi

The determination of surface coverage of adsorbate was calculated by measuring the integrated area below the voltammogram which represents the total charge Q. The total integrated area below the CV of the unmodified (clean) catalyst (Figure.2) can be considered as $\theta_{cat}= 1$. The decrease in the integrated area was attributed to adsorbate coverage. So the fractional adsorbate coverage can be determined by using the following equation:

$$Q_{ad} = \frac{Q_{clean} - Q_{\mathrm{mod}}}{Q_{clean}} \qquad (1)$$

where: θ_{ad} is the surface coverage of adsorbate in terms of $H_{UPD}{}^{*}$ sites blocked, $\mathbf{Q_{clean}}$is the total integrated charge for the clean catalyst, and $\mathbf{Q_{mod}}$is the total integrated charge for the modified catalyst (Figure 3). θ_{ad} may be considered as the fraction of free Pt sites remaining after adsorption.

$H_{UPD}{}^{*}$ = hydrogen under potential deposition corresponds to CV peaks in the range 0-0.3V (Pd/H). For polycrystalline Pt, this corresponds to 1 H atom per Pt site corresponding to a charge density of 220 µC cm^{-2}.

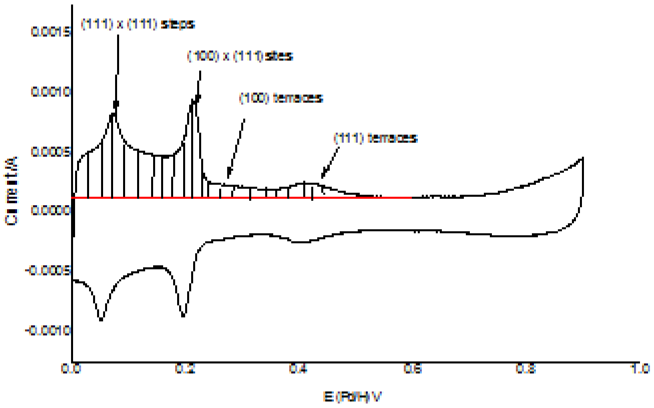

Figure 2: Voltammogram of the total integrated charge (shaded) for a clean Pt catalyst

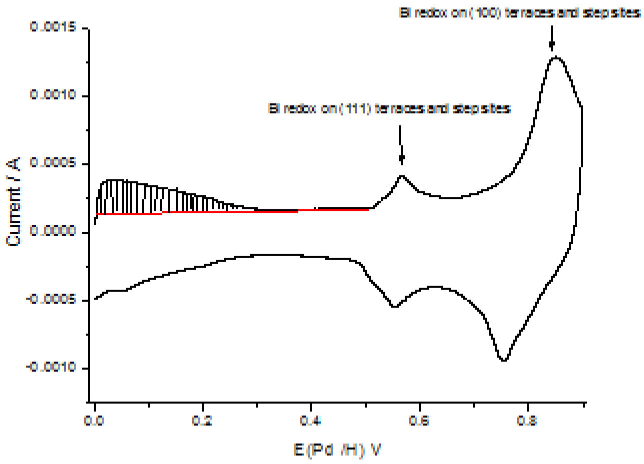

Figure 3: Voltammogram the total integrated charge (shaded) for bismuth modified Pt catalyst.

5. Results and Discussion

5.1 Adsorption of bismuth onto unsintered 5% Pt/G

Tables 1 and 2 show how the enantiomeric excess decreases as unsintered Pt/G was progressively load with bismuth using increasing amounts of $Bi(NO_3)_{3(aq)}$ as described in section 4.1. Figure 4 and 5 shows this data in graphical form.

Table 1: Effect of bismuth adsorption on enantiomeric excess in dichloromethane observed in ethyl pyruvate hydrogenation using CD-derivative and CN-derivative modified unsintered Pt/G catalyst with 1 ml of aqueous bismuth nitrate adsorbed on catalyst.

Entry	Dosing volume Bi/cm^3	Amount of modifiers (mg)	Enantiomeric excess (%) (R)	Conversion (%)	Time Minutes	Nominal rate mmol $g^{-1}h^{-1}$
1	1	5 CD-der	21.4	87	100	0.87
2	1	5 CN-der	27	90	54	1.67
3	1	10 CD-der	14.2	98	117	0.84
4	1	10 CN-der	31.4	95.1	50	1.9
5	1	15 CD-der	13	82	54	1.51
6	1	15 CN-der	24	98	71	1.38
7	1	20 CD-der	10.1	94	67	1.4
8	1	20 CN-der	29.4	83.4	71	1.17

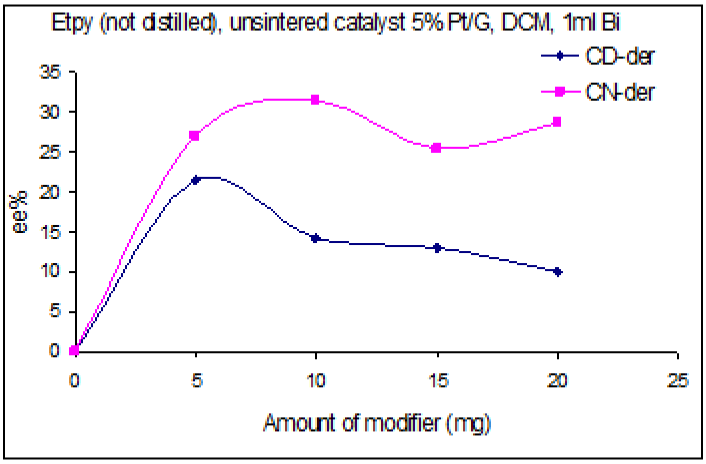

Figure 4: Enantiomeric excess in dichloromethane versus amount of modifier (mg).Unsintered 5% Pt/G catalyst with 1 ml of aqueous bismuth nitrate adsorbed on catalyst.

Table 2: Effect of bismuth adsorption on enantiomeric excess in dichloromethane observed in ethyl pyruvate hydrogenation using CD-derivative and CN-derivative modified unsinteredPt/G catalyst with 40 ml of aqueous bismuth nitrate adsorbed on catalyst.

Entry	Dosing volume Bi/cm^3	Amount of modifiers (mg)	Enantiomeric excess (%) (R)	Conversion (%)	Time Minutes	Nominal rate mmol g^{-1}h^{-1}
1	40	5CD-der	8	99.4	77	1.29
2	40	5CN-der	25	97	58	1.67
3	40	15CD-der	2.4	96	42	2.29
4	40	15CN-der	25.4	98	63	1.55
5	40	30CD-der	1.3	99	54	1.83
6	40	30CN-der	26.3	98.3	47	2.09
7	40	50CD-der	0.13	100	63	1.59
8	40	50CN-der	26	98	42	233

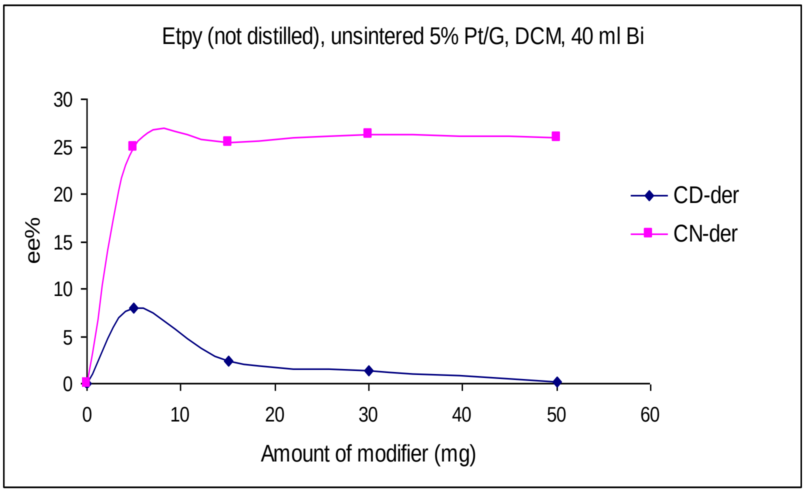

Figure 5: Enantiomeric excess in dichloromethane versus amount of modifier (mg).Unsintered 5% Pt/G catalyst with 40 ml of aqueous bismuth nitrate adsorbed on catalyst.

Some general trends may be observed from inspection of Figures 4 and 5. The addition of Bi to the unsintered catalyst has brought about a gradual decrease in *ee* using both CD-derivative and CN-derivative as modifiers although CN-derivative always gives rise to the greatest value of *ee* and both modifiers continue to provide an excess of the *R*-enantiomer. In order to illustrate this effect, the variation in *ee* for both CD-derivative and CN-derivative in dichloromethane as a function of Bi(NO$_3$)$_{3(aq)}$ dosing volume at fixed modifier amount (5 mg and 15mg) is shown in Figures 6 and 7. This data seems to suggest a loss of *ee* as Bi surface coverage increases. It will be recalled that this behaviour was also observed for Bi-modified 5% Pt/G catalyst using CD as chiral surface modifier [6]. In reference [6], CV was used to correlate Bi site adsorption with change in *ee*. In particular, the initial decrease in *ee* (and increase in rate) corresponded to blocking of defect sites such as steps and kinks whereas a lower overall *ee* was obtained from bismuth-free sites consisting of Pt{111} terraces [6].Therefore, CV was performed on the bismuth-modified catalysts to investigate if similar conclusions could be made in the present study.

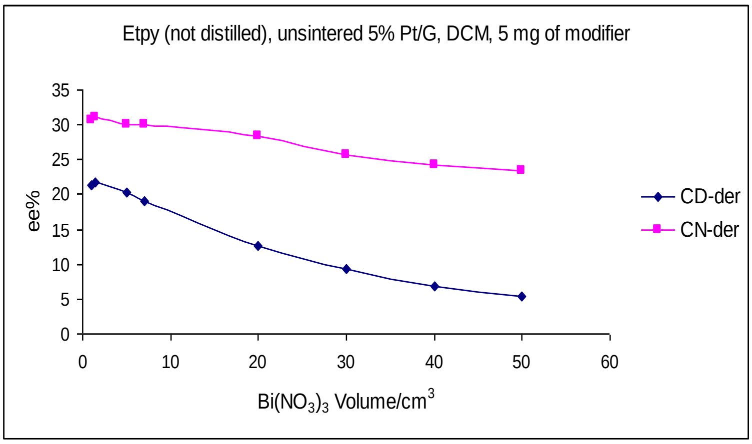

Figure 6: Adsorption of Bi on unsintered 5% Pt/G catalyst at 5 mg of modifier with 1, 1.5, 5, 7, 20, 30, 40 and 50 ml of aqueous bismuth nitrate adsorbed on catalyst.

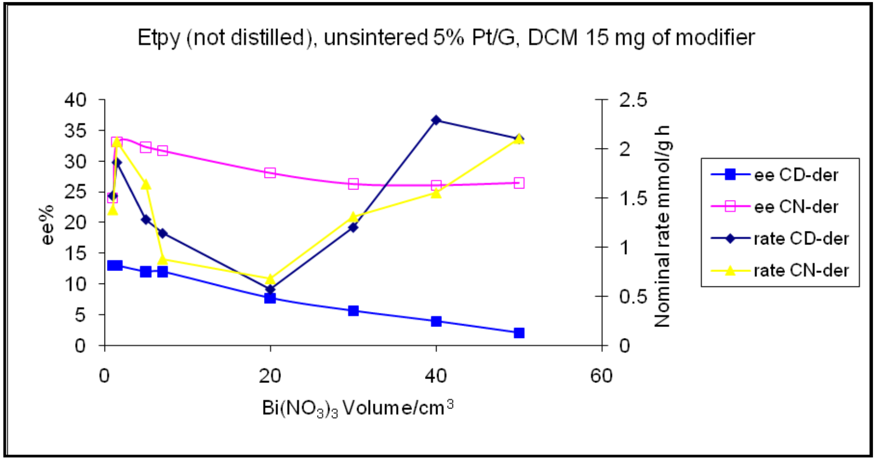

Figure.7: Hydrogenation of ethyl pyruvate. Nominal rate and enantiomeric excess versus the modifier concentration (unsintered 5% Pt/G catalyst in DCM).

From inspection of Figure 8, it is evident that, although Bi is present at the surface of the Pt, it is at very low concentration, even after dosing with 50 ml of aqueous $Bi(NO_3)_3$ solution. This may be deduced since there is absolutely no sign of Bi adsorption at Pt{111} sites, as would be signified by a sharp bismuth redox peak at 0.6V (Pd/H) [2]. In all studies of bismuth reported [11], defect and Pt{100} terraces are the first sites to be occupied followed by Pt{111} terraces between $0.4<\theta_{Bi}< 0.6$ monolayers equivalent of H_{UPD} charge [12]. Hence, the adsorption of bismuth was for some reason, strongly inhibited in this set of catalysts. That bismuth does occupy defect sites may be gleaned from decreases in the intensity of the H_{UPD} step peaks at 0.1 and 0.2V. Nonetheless, the CV results diverge somewhat from previous published work [6], particularly in relation to the systematic changes in H_{UPD} intensity expected as a function of Bi loading and corresponding increases in Bi-oxide features at 0.85V. Hence, it is possible that although measurements including CV and hydrogenation of etpy have been undertaken, the CV results indicate that for some reason bismuth was not being adsorbed properly on the catalyst surface. If it was due to some form of contamination one would also expect a decrease in rate. Clearly, the rate does decrease initially consistent with this proposal but it then begins to increase. That the decrease in rate can be unequivocally be ascribed to contamination may be seen by close inspection of Figure 8 in the potential region of the surface oxide (around 0.8V). It is seen that all CV curves exhibit a lower intensity than even clean Pt! Since addition of bismuth MUST increase intensity over and above Pt contribution in this potential range, this means that the Pt in these data is contaminated by adatoms other than bismuth. The increase in rate as > 20ml of Bi solution is added to the Pt would be consistent with small amounts of Bi being eventually adsorbed and hence a corresponding increase in rate is observed. No evidence for multilayer Bi was found in Figure 8 as this would give rise to electrochemical stripping peaks between 0V and 0.15V (Pd/H). Therefore, in order to achieve a proper, systematic variation (and to find agreement with previous studies) the Bi adsorbed on unsintered Pt catalysts were discarded and a fresh series of Bi-modified catalysts were prepared in which the unsintered 5% Pt/G catalyst was heated at 700K in hydrogen in order to clean the surface completely before dosing Bi.

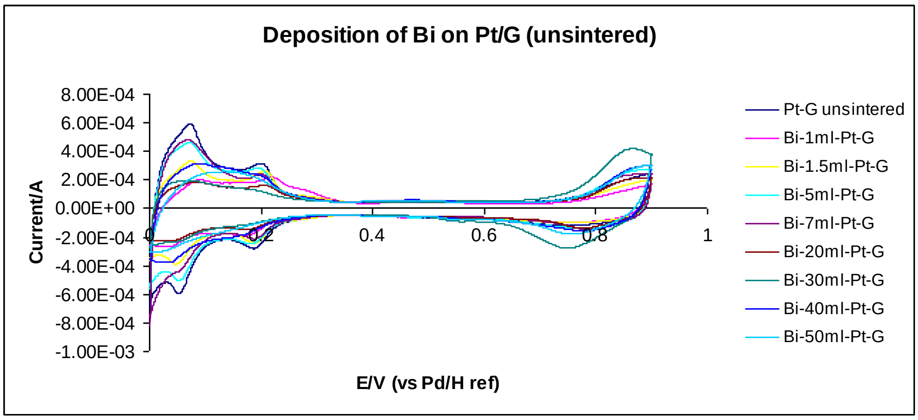

Figure 8:CVs of 5% Pt/G catalyst unsintered in 0.5M H2SO4. Sweep rate 50 mV s^{-1}.

5.2 Adsorption of bismuth onto 5% Pt/G at 700K

Table 3, 4 and 5 shows the effect of bismuth loading on *ee* and conversion for etpy hydrogenation in dichloromethane using CD-derivative and CN-derivative as modifiers. Figure 9,10 and 11 shows graphically the changes in *ee* as a function of both modifier amount and bismuth dosing. In contrast to the previous data for the unsintered catalyst, significant changes in the enantioselective excess are observed as bismuth loading is increased. The most striking observation is the inversion of *ee* as a function of bismuth loading for the CD-derivative modifier. Conversions are observed to be rather low, probably due to the decreasing amount of free Pt as bismuth is dosed onto the catalyst surface.

In Figure 12, the change in *ee* using CN-derivative and CD-derivative as modifiers is plotted for a constant modifier loading of 30mg and increasing amounts of bismuth. In Figure 13, the same plot is shown but with the variation altered for 5, 15 and 30 mg of modifier.

Table 3: Effect of Bismuth adsorption on enantiomeric excess in dichloromethane observed in ethyl pyruvate hydrogenation using CD-derivative and CN-derivative modified 5% Pt/G catalystsintered at 700K pre-treated with 1 ml ofaqueous bismuth nitrate adsorbed on catalyst.

Entry	Dosing volume Bi/cm^3	Amount of modifiers (mg)	Enantiomeric excess (%) (R)	Conversion (%)	Time Minutes	Nominal rate mmol $g^{-1}h^{-1}$
1	1	5 CD-der	13	15	42	0.36
2	1	5 CN-der	24	60	167*	0.36
3	1	15 CD-der	7.3	11.1	57	0.19
4	1	15 CN-der	30	20	167*	0.12
5	1	30 CD-der	3	15.1	47	0.32
6	1	30 CN-der	30.4	3	-	*

*- Possible leak on system for this data.
- N.A = Not available.

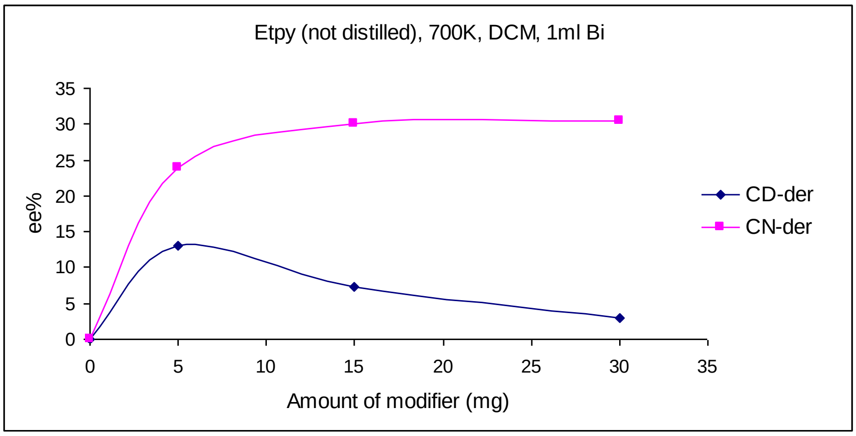

Figure 9: Enantiomeric excess in dichloromethane versus amount of modifier (mg). 5% Pt/G catalyst sintered at 700K with 1 ml of aqueous bismuth nitrate adsorbed on catalyst.

Table 4: Effect of Bismuth adsorption on enantiomeric excess in dichloromethane observed in ethyl pyruvate hydrogenation using CD-derivative and CN-derivative modified 5% Pt/G catalyst sintered at 700K pre-treated with 1.5 ml of aqueous bismuth nitrate adsorbed on catalyst.

Entry	Dosing volume Bi/cm^3	Amount of modifiers (mg)	Enantiomeric excess (%) (R)	Conversion (%)	Time Minutes	Nominal ratemmol g^{-1}h^{-1}
1	1.5	5 CD-der	5.2	10	63	0.16
2	1.5	5 CN-der	36	4	65	0.06
3	1.5	15 CD-der	3	7.4	58	0.13
4	1.5	15 CN-der	35.3	4.4	57	0.08
5	1.5	30 CD-der	1.4	5.2	48	0.11
6	1.5	30 CN-der	36	4	-	-

- N.A = Not available.

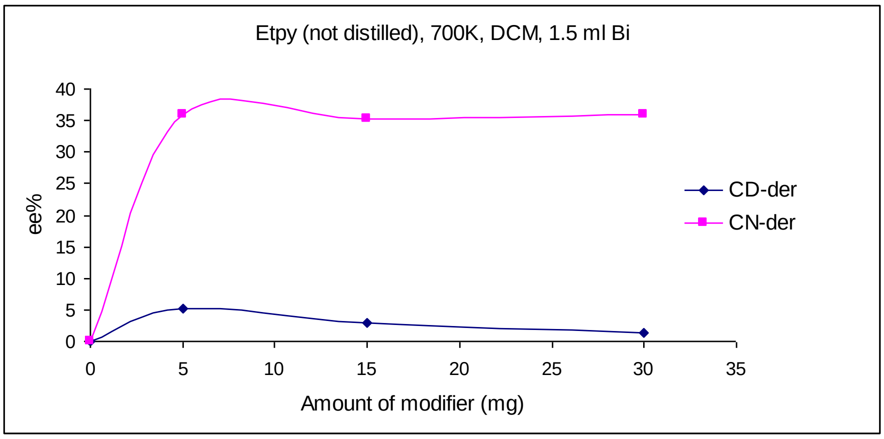

Figure 10: Enantiomeric excess in dichloromethane versus amount of modifier (mg). 5% Pt/G catalyst sintered at 700K with 1.5 ml of aqueous bismuth nitrate adsorbed on catalyst

Table 5 Effect of Bismuth adsorption on enantiomeric excess in dichloromethane observed in ethyl pyruvate hydrogenation using CD-derivative and CN-derivative modified 5% Pt/G catalyst sintered at 700K pre-treated with 40 ml of aqueous bismuth nitrate adsorbed on catalyst.

Entry	Dosing volume Bi/cm^3	Amount of modifiers (mg)	Enantiomeric excess (%)	Conversion (%)	Time Minutes	Nominal rate mmol $^{g-}$1h^{-1}
1	40	5 CD-der	19 (S)	2	58	0.03
2	40	5 CN-der	21 (R)	3	79	0.04
3	40	15 CD-der	26.2 (S)	10	56	0.18
4	40	15 CN-der	32 (R)	8.1	54	0.15
5	40	30 CD-der	24 (S)	8.2	-	-
6	40	30 CN-der	30 (R)	7.4	58	0.13

- N.A = Not available.

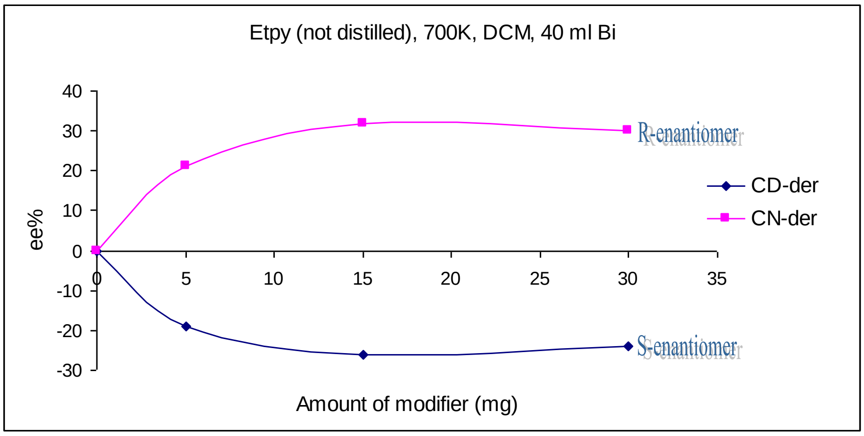

Figure 11: Enantiomeric excess in dichloromethane versus amount of modifier (mg). 5% Pt/G catalyst sintered at 700K with 40 ml of aqueous bismuth nitrate adsorbed on catalyst.

Inspection of Figure 12 and 13 indicates that optimal *ee* is obtained for a bismuth loading of between 20 and 30 cm^3 of bismuth solution and that this quantity of bismuth gives rise to a broad maximum in *ee* in the case of CN-derivative and a sharper maximum (but-opposite sign of *ee*) for the CD-derivative. Similar behaviour has been reported by

Hutchings *et al.*[10] for bismuth dosed Pt/Al_2O_3 catalysts and it was speculated that bismuth could be occupying step sites at low coverages but terrace sites at higher coverages, although no evidence for this speculation was presented. The rate of the reaction also appears to pass through a maximum at a similar stage of Bi dosing (Figure 11). This is consistent with previous results showing that when all defect sites are blocked, the vacant Pt{111} terraces give rise to a greater rate of reaction [12-13]. In Figure 12 are the CVs of the heated 700K/H_2 5% Pt/graphite catalyst collected as a function of bismuth dosage. It is evident that this data agrees completely with previous work reported by Jenkins *et. al.*[14] and Albdulrahman [6]. The initial bismuth adsorption is seen to occur at defect sites as exemplified by blocking of Pt{111}x{111} and Pt{111}x{100} step sites associated with H_{UPD} processes at 0.1V and 0.2V respectively. Subsequent adsorption may be seen to occur on Pt{111} terraces (blocking of broad peak between 0.3-0.5V and the growth in the well known bismuth redox peak at 0.6V previously ascribed to bismuth on Pt{111}) [13]. The corresponding bismuth oxide redox peak for steps/Pt{100} terraces at 0.85V is observed to increase in magnitude as a function of bismuth loading. Further inspection of Figure 14 indicates that complete blocking of step sites occurs between 20 and 30 cm^3 of bismuth dosed, precisely where the maximum values of *ee* are recorded as mentioned previously. Clearly the inversion of *ee* for CD-derivative being reached at this bismuth coverage is consistent with speculations from Hutchings *et al.* [10] that CD-derivative is being forced to occupy differing adsorption sites, probably terraces instead of defects. However we will return to this point later when CD and CN as modifiers are considered. The variation in H_{UPD} coverage/ θ_{Bi} as a function of bismuth dosing is presented in Table 7 based on equation (1) in section 6.1.

Table 6: Effect of Bismuth adsorption on enantiomeric excess in dichloromethane observed in ethyl pyruvate hydrogenation using CD-derivative and CN-derivative modified 5% Pt/G catalyst sintered at700K.

Dosing volume Bi/cm^3	5 CD-der (ee. %)	5 CN-der (ee %)	15 CD-der (ee %)	15 CN-der (ee %)	30 CD-der (ee %)	30CN-der (ee %)
1	13 (R)	24 (R)	7.3 (R)	30 (R)	3 (R)	30.4 (R)
1.5	5.2 (R)	36 (R)	3 (R)	35.3 (R)	1.4 (R)	36 (R)
5	3.3 (S)	20 (R)	12.3 (S)	35.3 (R)	13 (S)	34 (R)
7	6.1 (S)	28 (R)	19.2 (S)	35 (R)	17.4 (S)	35 (R)
20	25.3 (S)	37.2 (R)	28 (S)	40 (R)	28.1 (S)	39.4 (R)
30	21.4 (S)	36 (R)	34 (S)	42 (R)	33 (S)	42 (R)
40	19 (S)	21 (R)	26.2 (S)	32 (R)	24 (S)	30 (R)
50	16 (S)	21.4 (R)	19.3 (S)	25.4 (R)	14 (S)	26.4 (R)

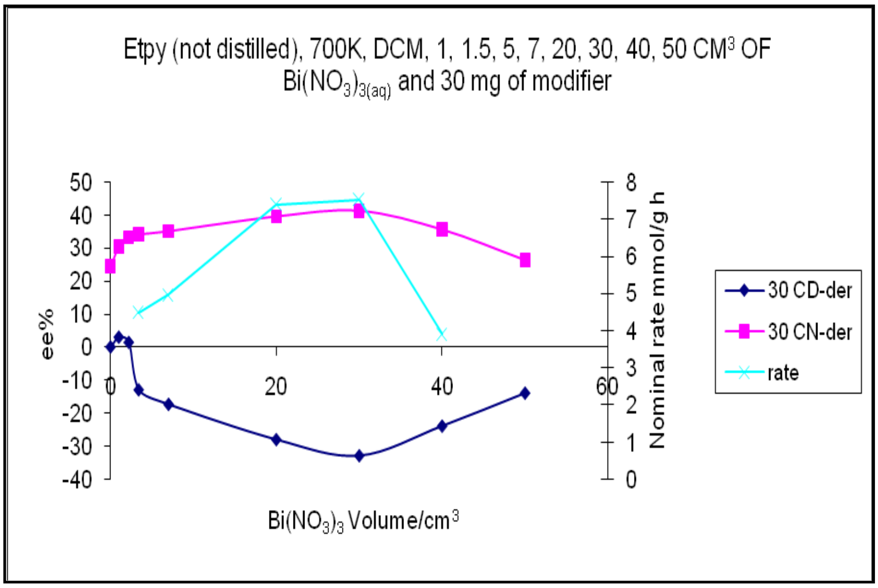

Figure.12: Adsorption of Bi on 5% Pt/G catalyst sintered at 700K and enantiomeric excess at 30 mg of modifier 1, 1.5, 5, 7, 20, 30, 40 and 50 ml of Bi solution. The variation in nominal rate is also depicted.

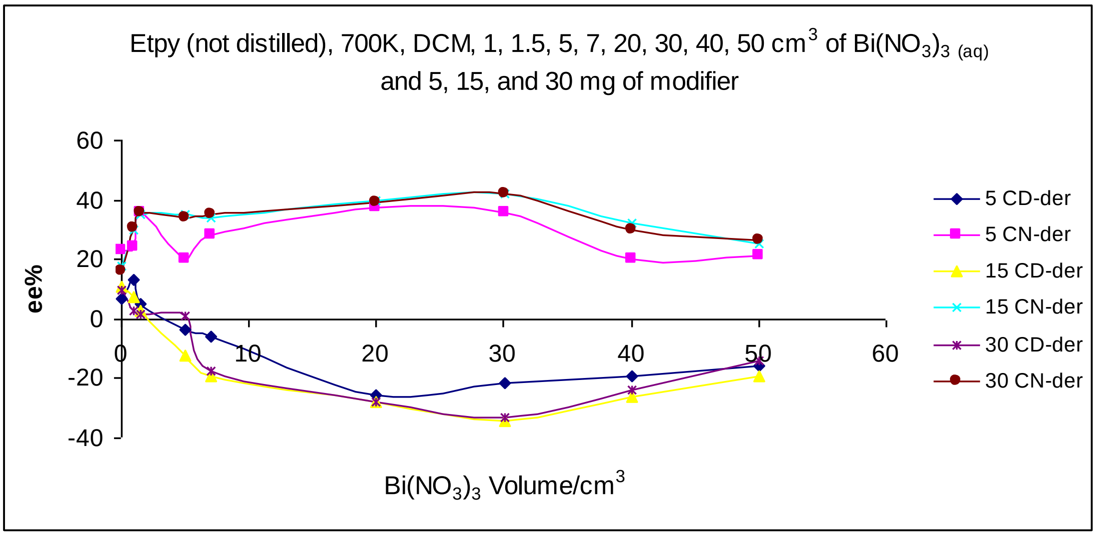

Figure 13: Enantiomeric excess in dichloromethane versus various concentration of bismuth with (CD-derivative and CN-derivative) modified 5% Pt/ G catalyst sintered at 700K.

Table 7: Dosing volumes of $Bi(NO_3)_3$ and surface coverages for 5% Pt /G catalyst sintered at 700K.

Entry	Dosing volume Bi/cm^3	Surface Coverage /θ_{Bi}
1	0.0	0.0
2	1	0.15
3	5	0.29
4	7	0.32
5	20	0.83
6	30	0.87
7	40	0.85
8	50	0.88

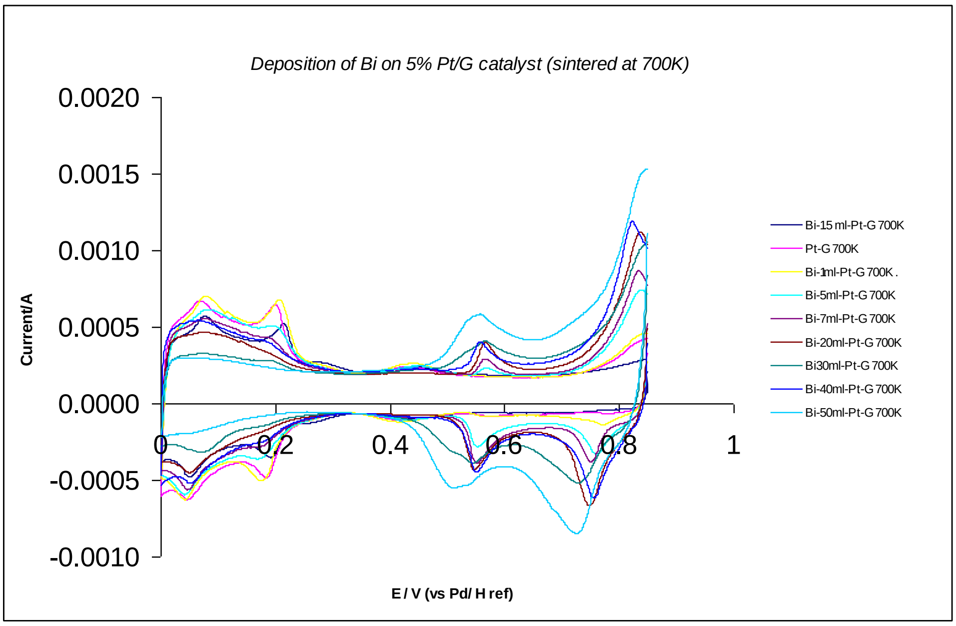

Figure 14: CVs of 5% Pt/G catalyst sintered at 700K in 0.5M H_2SO_4. Sweep rate 50 mV s^{-1}.

6. Conclusion

To sum up, it has been shown that the sense of enantio selectivity for the hydrogenation of ethyl pyruvate can be a function of the modifier concentration over ((Cinchonidine-derivative (CD-derivative)) and (Cinchonine-derivative (CN-derivative)). Furthermore, we have shown the effect of bismuth on the enantioselective hydrogenation of ethyl pyruvate over Pt/C surfaces from the results presented it appears that blockage of kink and step sites has a more significant effect on enantiomeric excess (*ee*) than blockage of terrace sires. In addition, when CD-deris added, this result in the formation of the R-enantiomers. Whereas, when low amounts of Bi are added to defects the result of enantioselectivity changed. Hence we conclude that the CD-der adsorbed at defect sites gives rise to R-enantiomers.

Whereas, CD-der adsorbed at (111) terrace sites (when Bi blocks all defects) give rise to S-enantiomers. This conclusion confirms speculations in the recent paper by Hutchings et al [10].

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