



## A Combined Electrochemical and Catalytic Study of The Enantioselective Hydrogenation of Ethyl Pyruvate at Supported Platinum Nanoparticles: Effects of Pd Adsorption

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**Abstract** - The enantioselective hydrogenation of ethyl pyruvate (etpy) has been studied over cinchonidine-modified 5% Pt/graphite (Pt/G) as a function of Pd adsorption. The effect of adsorbed Pd coverage on reaction rate and enantiomeric excess (ee) has been examined in detail. Adsorption of Pd onto Pt/G resulted in preferential decoration of Pt step sites followed by subsequent adsorption of Pd at Pt{111} terraces. This resulted in a mark decrease in both ee and reaction rate up to one monolayer of Pd.

Un-sintered Pt/G was 5 wt% of Pt supported on graphite, with a mean Pt particle size of 14 nm. Thermal annealing and sintering of catalyst was performed at 700 K in a continuous flow of 5% H<sub>2</sub>/Ar followed by deposition of Pd on the Pt nanoparticles surface. The coverage of Pd could be determined from integration of the voltammetric charge in the range 0 - 0.3 V. Enantioselective hydrogenation of etpy was carried out in a stirred 100 ml Baskerville autoclave reactor under the following conditions: 30 bar of H<sub>2</sub> pressure, 250 mg catalyst, 20 mg Cinchonidine (CD), 20 mmol etpy, 12 ml dichloromethane, and agitator speed 1000 rpm. All reactions were performed at room temperature.

Voltammograms illustrating the effect of Pd adsorption on Pt/G are shown in Figure 1. At low coverage, Pd adsorption was occurred at {110} and {100} step/kink sites [1]. As Pd coverage increases, a sharp Pd electrosorption peak at 0.17 V was observed characteristic of Pd adsorb on Pt{111} terraces [2] and the clean surface features were further attenuated. Upon approaching and exceeding one monolayer of palladium, a second Pd peak was observed at 0.21 V [2,3].

Adsorption of Pd on the Pt/G catalysts inhibited the rate of etpy hydrogenation significantly. It was found that the higher the Pd coverage, the slower the reaction proceeded, as shown in Figure 2. The decrease in reaction rate was marked in the coverage region of  $\theta_{Pd} = 0 - 0.72$ , whereas it remained almost constant at coverage of  $\theta_{Pd} = 0.72 - 4.8$ . The decrease in reaction rate was attributed by Wells *et al.* to the formed intermediates showing no indication of forming hydrogen bonds to the quinuclidine-N atom of the modifier [4]. Baiker and co-workers also reported [5] that hydrogenation of etpy over CD modified Pd-Pt/alumina decreased both reaction rate and ee. We speculate that the known stability of enolic surface intermediates on Pd relative to Pt may be the cause of this rate decrease.

Figure 3 showed that Pd adsorption reduced the ee from 57.3 to 1.5 % at high Pd coverage. The most significant decrease in ee was coincident with the blockage of kink/step sites. Ee clearly mimics the rate behavior outlined in Figure 2. This behavior is similar to that found with of Bi-modified Pt catalysts [1]. The decrease in ee when Pd was used was attributed to Pd acting as a step/kink site blocker and to Pd catalysed reaction forming S-enantiomer preferentially [4].

Finally, It should be noted that effect of Pd adsorption on the enantioselectivity was mainly associated with step/kink sites. Therefore we suggest that these sites are the most important for enantioselectivity on Pt undergoing Orito-type reactions.

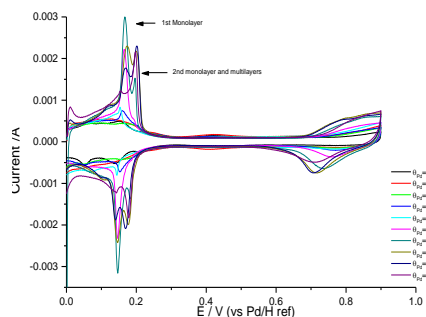


Fig. 1. CVs of Pd modified Pt/G. Sweep rate 10 mV s<sup>-1</sup>.

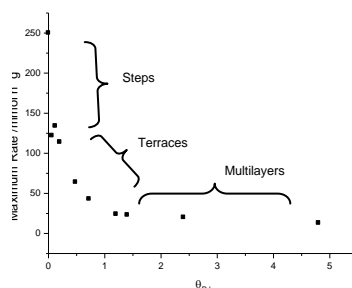


Fig. 2. rate versus Pd coverage.

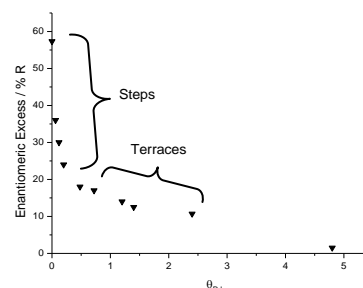


Fig. 3. ee versus coverage.

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