The use of ligands to determine the origin of selectivity in the hydrogenation of acetylene:ethylene mixtures.

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Introduction

The removal of trace acetylene from ethylene streams is the most vital step in obtaining commercially valuable stocks of the world's most produced organic compound[1]. Under industrial conditions carbon monoxide is used as a competitve adsorbate in the gas stream and enhances selectivity by lowering the surface availibility of ethylene and hydrogen[2]. The presence of CO together with a limited hydrogen supply are however indisputably linked to increased oligomer formation and accelerated catalyst deactivation[3]. Modified catalysts for this reaction are primarily bimetallic catalysts, typically silver-palladium alloys but non precious metal catalysts have also been developed including the recently published work by Studt et al.[4]. In the main, the source of selectivity is attributed to either reduced active ensemble size effects or altered electronic characteristics of the active metal. Unfortuantely, with alloyed metals, these two effects are indistinct. Indeed further theories attribute selective behaviour to the availablity of sub-surface hydrogen.[5] The logic behind our experiments is that, by using ligands, one can exaggerate steric or electronic effects by careful consideration of the ligand chosen and thereby assess the mode in which selectivity is primarily achieved. To the best of our knowledge this is the first time this method of modification has been studied in this particular reaction.

Materials and Methods

Pd/TiO_2 (degussa P25) catalyst was prepared by dropwise impreganation using $Pd(NO_3)_2$ as precursor. The ligand modification was carried out by solvent impregnation and the performance was studied using a variety of techniques including thermogravimetric analysis, temperature programmed desorption, chemisorption, diffuse reflectance IR and fixed bed reactor studies. The ligand modifiers used were triphenylphosphine (PPh_3) and phenyl sulfide (Ph_2S) and in most cases were deposited in an excess relative to the amount of metal. Due to the limited sensitivity of some of these techniques the catalysts used were 1 or 2 % wt. palladium. It is the case that commercial catalysts use significantly lower loading in the order of < 0.1 % wt. palladium which results in low loadings and a high dispersion of very small particles which inevitably affects selectivity. Following characterisation of our 1 and 2 % catalysts it is our aim to run the commercial catalyst using similar modifications to further investigate the corroborative effect of these conditions.

Results and Discussion

Reactions were carried out in an excess of hydrogen and in the absence of CO to isolate the selective effect of the modifier on the reaction. It was found that under isothermal reaction conditions the modified catalysts demonstrated significantly higher selectivity than the unmodified Pd/TiO_2, even to 99% conversion of the acetylene. Both phenyl sulfide and triphenylphosphine are expected to bind strongly through their metal atom and create a large steric hindrance on the surface of the Pd particles. Figure 1 a) presents the CO adsorption observed on all catalysts by DRIFTS after subtraction of the gas phase and background signals. The unmodified catalyst and lower ratio modified catalyst (1:4 PPh_3:Pd) demonstrate an extra binding signal which has been assigned to bridged CO species adsorbed on the Pd (100) plane[6]. This plane has been attributed responsibility for the formation of carbided species and direct hydrogenation from acetylene to ethane[7]. It is suggested therefore that the eradication of this site is a source of selectivity in the reaction. In the case of the sulfide ligand it has also been possible to decompose the structure to benzene and a sulfided palladium species. It was observed using a combination of TGA and DRIFTS that in the absence of the aromatic portion of the ligand the selectivity drops off significantly but is however still superior to the unmodified catalyst. The sulfur ligand is expected to have a much more pronounced electronic effect on the metal than the phosphorus ligand. Further studies will elucidate whether the electronic effect is necessary to selectivity or if site blocking is the only major contributing factor.

Significance

This study promises the possibility of highlighting the essential component of a catalyst in order to selectively hydrogenate acetylene in the presence of ethylene. The catalysts prepared so far demonstrate very minimal ethylene loss (<5%) under conditions where full hydrogenation should be favourable *i.e.* excess hydrogen.

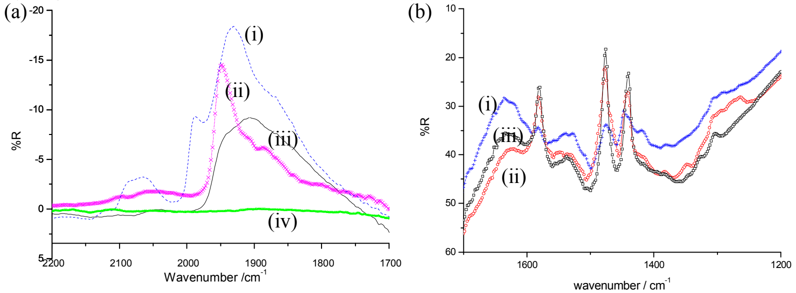

Figure 1. a) IR spectra of CO adsorption on (i) 1:4 PPh_3:Pd, (ii) 2.5:1 PPh_3:Pd (iii) 2.5:1 Ph_2S:Pd (iv) 2.5:1 Ph_2S:Pd (after decomposition). b) IR spectra of aromatic region on Ph_2S catalyst (i) reduced at 120 ºC (ligand decomposed) (ii) reduced at 50 ºC (iii) not reduced.

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