Comment

On Pd carbide formation and vinyl acetate synthesis

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Han *et al.* [1] recently showed that the formation of carbide is of significance for VAM synthesis on Pd and Au/Pd alloy catalysts. They reported that bulk PdC can form during vinyl acetate synthesis, resulting in catalyst deactivation, and that alloying with Au appears to suppress this effect. The purpose of this note is to support this notion with recent data of our own. Our work has been conducted solely on single crystals, not on high area catalysts which Han *et al.* [1] used. Nonetheless, we arrive at similar conclusions regarding the importance of carbide formation and the possible role of Au [Bowker *et al.*submitted; 2]. We have investigated the adsorption, desorption and reaction of a number of relevant organics on Pd(110), including ethene (Bowker *et al.*, submitted), acetic acid, vinyl acetate and even acetaldehyde [3]. The important point here is that the Pd (110) surface manifests somewhat surprising behaviour, that is, above 450 K all of these molecules appear to adsorb continuously with high probability (measured using a molecular beam reactor [4]), even when many monolayers of carbon have been deposited. Thus, as shown in figure 1, ethene continues to adsorb with a probability of 0.54 at 573 K even after an extended time experiment when 10 monolayers of carbon have been deposited on the surface. The same type of behaviour applies to the other molecules shown above and the overall reactions are as follows, where Ca refers to the deposited carbon, and it is likely to be representative of a general class of bebaviour for organics on Pd–

$$C_2H_4 \rightarrow 2H_2 + 2Ca$$
$$CH_3CHO \rightarrow 2H_2 + CO + Ca$$
$$CH_3COOH \rightarrow 2H_2 + CO_2 + Ca$$
$$CH_3COOC_2H_3 \rightarrow 3H_2 + CO_2 + 3Ca$$

Below the critical temperature of 450 K at which continuous C deposition and hydrogen evolution from ethene occurs, the adsorption saturates, above this temperature continuous sticking is observed. Below 380 K the total uptake is ~0.25 monolayers of molecules (0.5 monolayers of carbon), though the coverage at saturation is higher between 400 and 450 K, due, we believe, to the build-up of carbon in the immediate subsurface region and limited bulk diffusion.

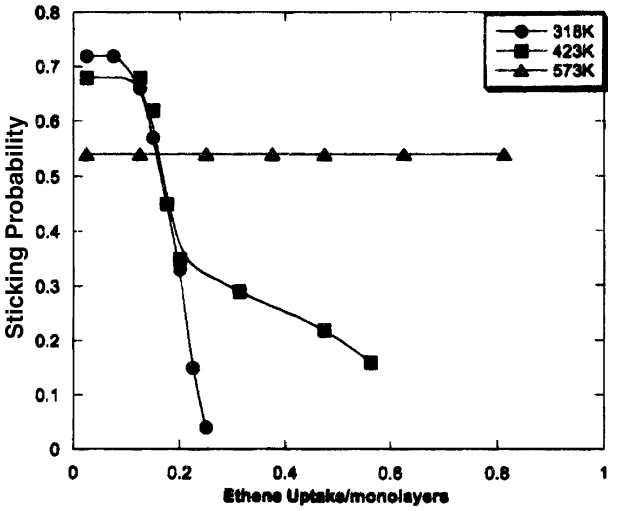

Figure 1. Results from the molecular beam reactor for ethene adsorption on Pd(110) at three surface temperatures. Above 450 K ethene continues to adsorb on the surface with high probability, even though the molecule decomposes to release hydrogen into the gas phase and deposit carbon atoms on the surface. The carbon does not poison the reaction because it diffuses subsurface.

In our recent paper [3] we tentatively proposed that the role of Au might be to (i) suppress the carbidisation and hence deactivation of the Pd, and we went on to suggest that (ii) this in turn would result in reduced dehydrogenation reactions, thus favouring selective acetoxylation. The work of Han *et al.* [1] shows very clear evidence that at least the first assertion appears to be correct.

References

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