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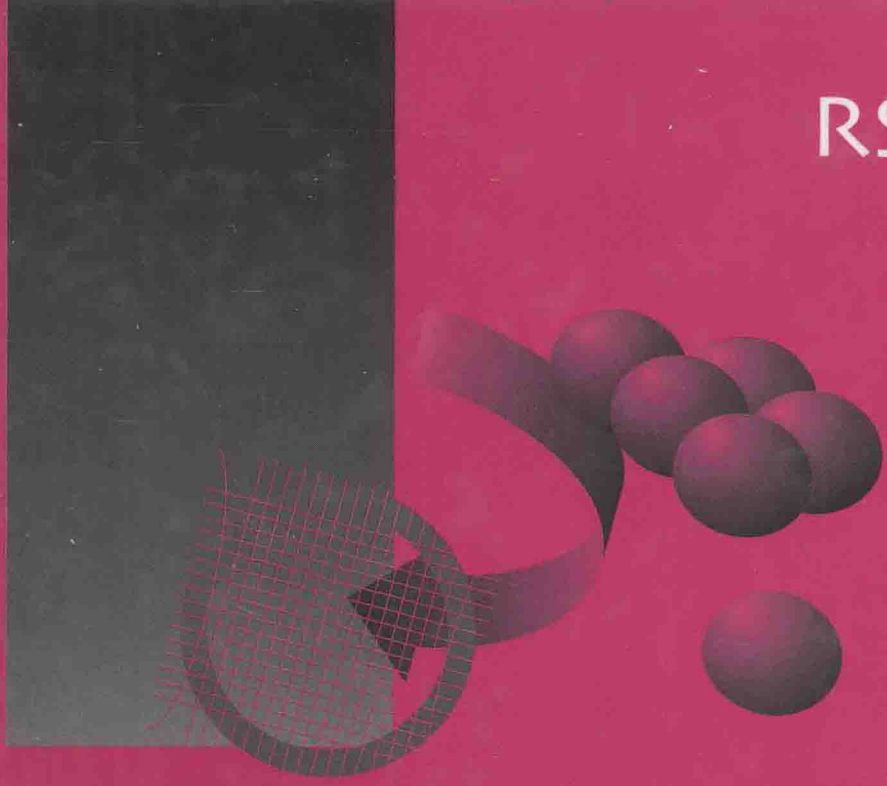

catalysis in application

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Catalysis in Application

Preface

Catalysis in Application contains a selection of papers presented at the International Symposium on Applied Catalysis held at the University of Glasgow from 16–18 July 2003. The Symposium was a joint meeting of Surface Reactivity & Catalysis, Applied Catalysis and Process Technology subject groups of the Royal Society of Chemistry and the Institution of Chemical Engineers. The meeting also marked the retirement of Professor Geoff Webb after nearly 40 years active participation in catalysis research. The content of the meeting was focused around hydrogenation, deactivation, chiral catalysis and environmental catalysis, four areas that Geoff has made significant contributions to during his career. The meeting was attended by delegates from industrial and academic laboratories throughout the UK, Europe, USA and Asia.

Over the course of Geoff's career, catalysis has made significant advances, for example when he started in Glasgow the ICI Low Pressure Methanol process using $Cu/ZnO/Al_2O_3$ catalysts had not been invented. In the 60s and 70s new catalysts and catalytic processes changed the face of petrochemical and refinery processing. In the 80s and 90s the move for catalysis was into fine chemicals and pharmaceutical conversions. The application of catalysis has increased, such that catalysts are responsible for the manufacture or processing of a large number of products in daily use (from clothes to all plastic products), to preserving our environment and health (enabling a sustainable production, energy and mobility), to enabling the development of advanced and functional materials and devices. Even so, catalysis is still in its infancy, the simple problems have been solved, if not fully understood, but major challenges lie ahead. The development of highly selective catalysts for complex chemical transformations is a constant industrial driver. However advances in catalysis rarely come from a single discipline. The complexity of the catalytic process usually requires that chemistry and engineering intimately mix to deliver the desired effect. The need for a multi-disciplinary approach is reflected in this symposium.

The organisers would like to express their thanks to the participants and to the authors for their commitment to submitting camera-ready manuscripts on time. Finally we would like to thank all the people who have worked hard behind the scenes to enable this conference to take place and these proceedings to be published.

S. David Jackson
Justin S. J. Hargreaves
David Lennon

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MODIFICATION OF CATALYSIS AND SURFACE REACTIONS BY SURFACE CARBON

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1 INTRODUCTION

This paper is devoted to considerations of the role of surface carbon in modifying surface reactivity, an area to which Geoff Webb has contributed significantly during his career [1,2]. It is generally considered that surface carbon is a poison for many reactions. Indeed, in the strict sense this is usually true (that is, as carbon builds up on a surface and total activity goes down). However, in this paper we give some examples of surface reactivity which show that carbon can have a very positive role to play in manipulating reaction selectivity, so much so that it can result in ***higher activity to desired products.***

Geoff Webb has been involved in this area during his years of contribution to the field of surface reactivity and catalysis. In particular he noted that the presence of carbon on metal surfaces may take a direct role in the catalysis of butene hydrogenation, by acting as a surface hydrogen exchange medium between hydrogen in the gas phase and the adsorbed olefin [2]. These kinds of ideas were extended by Somorjai [3] and others to hydrocarbon reactivity on surfaces by identifying the presence of certain intermediates on the surface (e.g. ethylidyne [4]). He also recognised that, although the metal surface can contain a very large amount of surface C, nevertheless hydrocarbon reactions can still proceed at a very high rate. In that case it was proposed that the reaction proceeds on the small amount of free surface still available [3].

Finally, a very nice example of the modification of surface reactivity by a surface poison is the case of methanol decomposition on Ni(100) studied by Johnson and Madix [5]. The clean Ni surface is a complete dehydrogenator, whereas the surface dosed with half a monolayer of S in an ordered structure results in a surface which is very selective to formaldehyde production, that is, the total dehydrogenation pathway is effectively blocked.

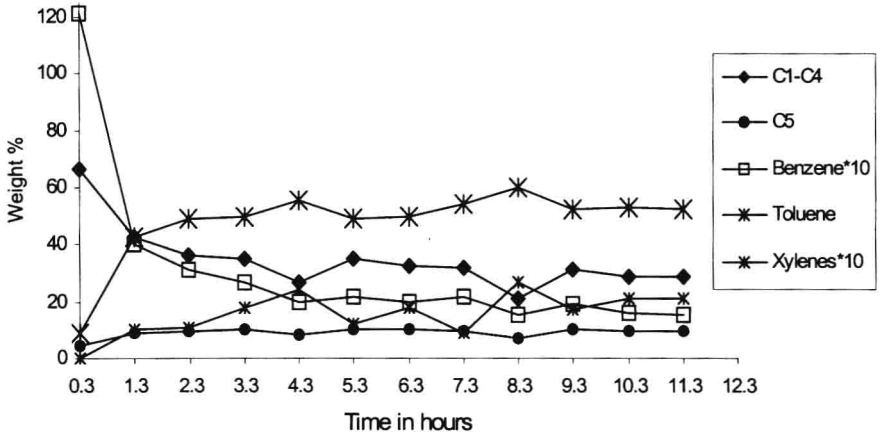
In what follows we show three very different examples of the influence of surface carbon on surface reactivity, namely, hydrocarbon reforming, the decomposition of a

carboxylic acid and the decarbonylation of acrolein. In each case it can be argued that the adsorbed carbon layer plays a positive role in the catalytic reactions involved.

2 HEPTANE REFORMING ON Pt-Sn CATALYSTS

Coking is generally thought to be a problem in hydrocarbon reforming catalysis, but it is not so widely recognised that it is essential to the successful operation of modern catalysts for producing high octane fuel. Thus fig 1 shows data for the reforming of n-heptane on an alumina-supported Pt-Sn catalyst with 0.3 wt% of each of the latter components. Here it can be seen that, as the coke builds up on the catalyst, so the selectivity to toluene, a much desired reaction due to the high octane rating of toluene, increases significantly. The important coke layer is built up within a very short time on stream and our estimates indicate that it corresponds to about 1 monolayer of 'coke' spread over the whole catalyst, most of it therefore being located on the support. In fact, we believe that 'coke' is an inappropriate description of what is likely to be a well-defined, evenly spread layer. This layer on the support, then, appears essential to the good performance of these catalysts. This level of surface carbon is nearly constant for a significant time of the run (between 0.3 – 10 hours on stream). There is then evidence that, at much longer times, multilayer carbon builds up which is more properly described as 'coke'. Although we didn't carry out long-term tests, there was 2.2 wt% coke after 5 hrs on stream and others report an acceleration of coking after a long time on stream. This appears to be a second stage of detrimental carbon deposition and is part of the reason for recycling the catalysts for carbon removal in an oxidation step in industry. In summary then, carbon deposition is essential for the good performance of industrial naphtha reforming catalysts.

a)



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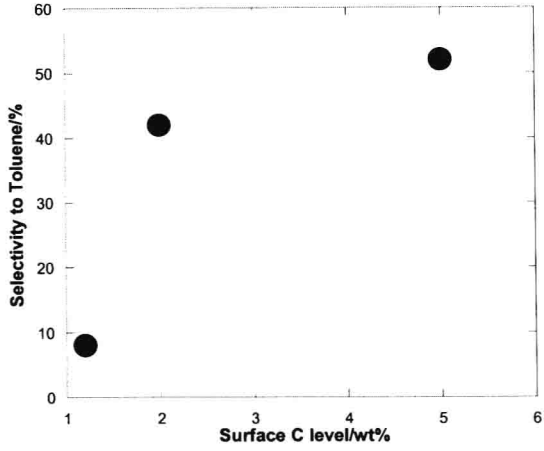

Figure 1 *a) Showing the change in reaction products with time for heptane reforming on a Pt-Sn catalyst which can be used for naphtha reforming. The 'fresh' catalyst predominantly exhibits hydrogenolysis to C1-C4 alkanes, whereas with time and coke build-up, it becomes very selective to aromatisation to toluene. b) The dependence of toluene selectivity upon coke level. Reaction conditions: temperature 515°C, H2:Heptane ratio = 3.7, heptane flow 4 mls liquid* hr^{-1}

3 THE ROLE OF SURFACE CARBON IN MODIFYING SURFACE REACTIVITY ON Pd(110)

3.1 Acetic Acid Decomposition on Pd(110)

Acetic acid decomposes on the clean surface at elevated temperature to produce gas phase CO_2 and hydrogen and leaves C (henceforth C_a for adsorbed carbon) on the surface [6,7]. However, this carbon has a surprising property, that is, it can modify the reaction pathway on the surface, yet does not affect the activity for adsorption very significantly. The C_a forms a well-ordered c(2x2) structure which is identified by LEED. As shown in fig 2 the carbon acts as a poison in one sense and in one regime of temperature, that is, it deactivates the surface for acetate decomposition in such a way that the acetate TPD peak is shifted from ~360-390K to 455K when the c(2x2) layer is preformed before dosing the acetic acid onto the surface. The overall reaction is –

$$CH_3COOH \rightarrow CO_2 + 2H_2 + C_a$$

Even though the C_a is there it does not poison acetate formation, which appears to occur with a similar adsorption probability, but it does stabilise it towards decomposition. In fact the desorption at 455K, occurring in the presence of C_a, is what is known as a 'surface explosion' [8], an autocatalytic decomposition, showing a very narrow half-width for the peak and anomalous desorption kinetics.

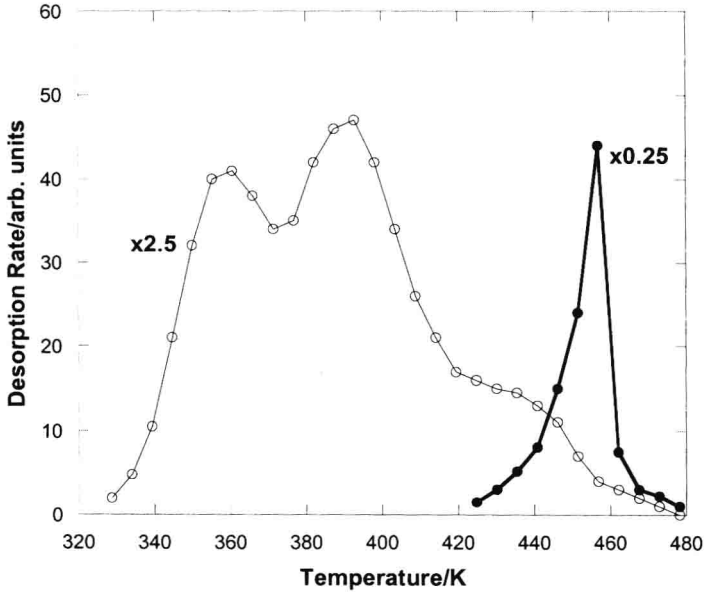

Figure 2 *Temperature programmed desorption experiment after acetic acid adsorption on Pd(110): a) on the clean surface and b) on the surface predosed with half a monolayer of C atoms in the c(2x2) structure*

When the reaction is carried out above 430K or so, then the reaction occurs at steady-state, notwithstanding the fact that a c(2x2) layer of carbon is present on the surface and that C_a is continually being deposited on the surface (fig. 3). The extra C_a appears to dissolve through the half monolayer of surface C into the bulk, presumably as a carbide. On the timescale of these experiments approximately 6 monolayers of C_a are deposited into the crystal with no apparent detriment to the reaction. In this regime the reaction does not appear to be limited by the surface C_a, that is, no net activation barrier is apparent and the rate is flux-limited. Presumably, if the pressure were much higher, then the surface would become populated by the stabilised acetate, which would then block sites and self-limit the reaction rate.

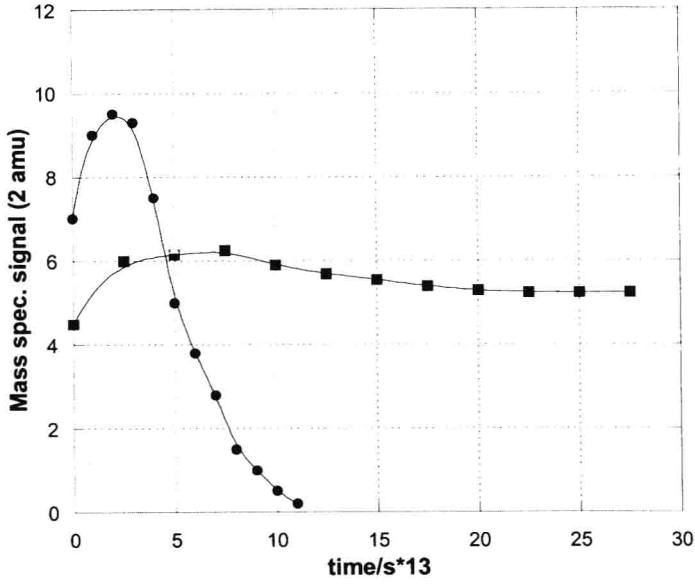

Figure 3 *Evolution of reaction products with time measured in the molecular beam reactor. At 423K(filled circles) hydrogen is evolved and stabilised acetate build-up on the surface, eventually blocking it to further reaction, whereas at 473K (squares) the acetate is unstable and the reaction proceeds at steady state on the c(2x2)-C layer*

3.2 Acrolein Decomposition on Pd(110)

This reaction shows a selectivity influence of adsorbed carbon on the decomposition reaction. If the acrolein is adsorbed at room temperature, then the molecule dehydrogenates to yield hydrogen in the gas phase and a mix of adsorbed CO and CHx species and then ceases due to blockage of the reaction sites by the latter. If the reaction is carried out at a slightly higher temperature then the reaction selectivity is changed. The surface is no longer a dehydrogenator and instead shows high activity and selectivity for the decarbonylation reaction (fig 4) , that is,

$$CH_2CHCHO \rightarrow C_2H_4 + CO$$

This reaction only occurs on the C-passivated surface and is selective in a limited temperature range; if the crystal temperature is > 350K, then dehydrogenation activity is seen again, presumably because extra C can be formed which can diffuse into the sub-

surface region as for the acetic acid decomposition above. If the surface is pre-dosed with carbon, then the decarbonylation reaction begins immediately at high rate.

Thus C plays a very important role as a reaction modifier here. It reduces the dehydrogenation ability of the Pd and instead facilitates hydrogen intramolecular mobility. It must be noted that the decarbonylation reaction is thermodynamically well-favoured, but dehydrogenation is even more preferred on the clean surface.

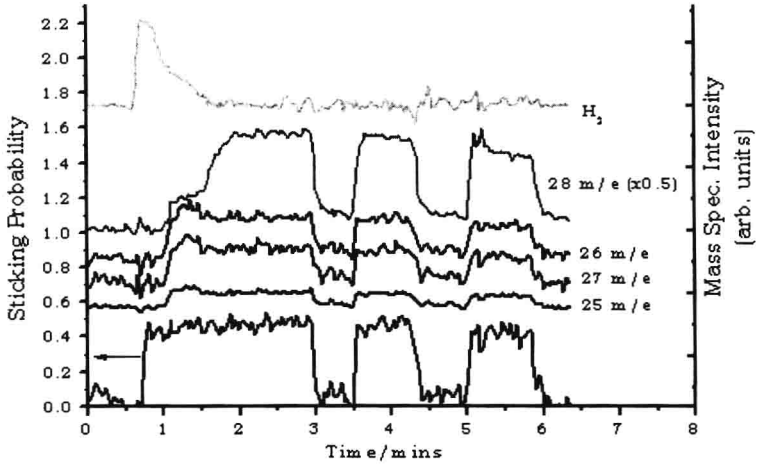

Figure 4 *A molecular beam reactor experiment in which the carbon-precovered Pd(110) surface is exposed to acrolein at313K, beginning upon opening the beam shutter at 0.7 minutes into the experiment. The surface shows a high adsorptivity for the acrolein (s~0.4) and steady stare reactivity after 1.5minutes to the decarbonylation of the acrolein, producing ethene and CO. The beam is blocked and re-opened at 3-3.5 and 4.3 to 5 minutes to check background signals. The experiment is stopped at 5.8 mins*

4 CONCLUSIONS

We have given three examples of reactions where the nature of the surface is significantly changed by the presence of surface carbon. For hydrocarbon reforming the presence of a monolayer of carbon, mostly on the support, plays a very positive role in suppressing the hydrogenolysis reactions and enhances the rate of the desired aromatisation reactions. For acetic acid decomposition, there is little evidence of deactivation of the surface when a half monolayer of carbon is adsorbed, the reaction probability still being very high. In the case of acrolein, surface carbon changes the reaction from total cracking of hydrogen from the molecule to steady-state decarbonylation, occurring in a very clean fashion with very high reaction probability.

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CATALYTIC PROPERTIES OF THE PLATINUM–HYDROGEN–CARBON SYSTEM

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1 INTRODUCTION

Pt catalysts are, as a rule, covered by "hydrocarbonaceous overlayers" during hydrocarbon reactions.[1] Their presence is necessary for steady-state activity in aromatization, C_5-cyclization, isomerization of alkanes.[2] Freshly regenerated catalysts (in a "Pt–H" state) exhibit high activity in hydrogenolysis. They become a *platinum-hydrogen-carbon* system, "Pt–C–H", after a short contact time with the reaction mixture.[2] The hydrocarbonaceous "Pt–C–H" entities correspond to the "reversible"[3] or to the "beneficial" carbon.[4] Catalyst after deactivation is transformed into "Pt–C".[2] Radiotracer methods can detect carbonaceous residues directly.[5–7] Hydrocarbonaceous deposits lose hydrogen and transform into "carbon" upon evacuation necessary for analysis by electron spectroscopy.[3] This may explain why relatively much C was detected by these methods.[8,9] Indirect methods involve carbon removal by oxidation[10,11] or hydrogenation.[2,12–14] Hydrogen treatment removed about 1 C atom per surface Pt.[13] Studies with ^{14}C radiotracer[6] showed ~0.7 C/Pt(surf.) after alkane exposures without hydrogen. This dropped to 0.15–0.20 C/Pt even in small H_2 excess. X-ray Photoelectron Spectroscopy (XPS) detected "massive" – graphitic and polymeric – carbon up to ~50% surface C after exposure to *t,t*-hexa-2,4-diene at 600 to 660 K.[15] Disordered C and ordered graphite layers on Pt were observed by lattice resolution transmission electron microscopy (TEM).[15] Exposure to hexane resulted also in similar amount and state of surface carbon.[16] "Regeneration" with O_2 and H_2 decreased the amount of "massive carbon", increasing the abundance of single C atoms or CH_x entities.[16]

The primary products of alkane reactions on Pt are dissociated alkyl radicals that give either reaction products or dehydrogenate further to form carbonaceous deposits.[17] They coexist with chemisorbed hydrogen, the abundance of which is, in turn, determined by the H_2 pressure, $p(H_2)$. Their competition results in maximum turnover rates[18,19] as a function of $p(H_2)$. Aromatization and dehydrogenation are preferred under small $p(H_2)$ values, together with "coking". A "polyene" route of coking[19,20] involves polymerization of *trans*-unsaturated intermediates whereas the "C_1 route"[11,21] would involve polymerization of the single C-atom entities. The deactivating effect of surface carbon depends on its amount and nature[15,16] and influences various reactions to a different extent. Catalysts representing platinum–hydrogen–carbon systems were obtained by intentional deactivating treatments of Pt. We report on their catalytic behaviour in hexane transformation, using this reaction itself as an indicator on the surface state of the catalyst.