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ALLOYING IN PLATINUM-BASED CATALYSTS FOR GASOLINE REFORMING: A GENERAL STRUCTURAL PROPOSAL

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Platinum/alumina catalysts have been used for many years in the process of gasoline octane upgrading normally referred to as reforming. It is now standard industrial practice to add another element to the catalyst, which may be chosen from many parts of the periodic table, and which acts to prolong the life and improve the selectivity of the catalyst. Additives in use include gallium, germanium, iridium, tin, rhenium and chromium. It is proposed that each of these components alloys with the platinum, but in such a way that the exposed surface of the catalyst particles continues to be wholly platinum. The alloying element is enriched in the immediate subsurface layer, and modifies the properties of the catalyst through an electronic interaction.

Keywords: Platinum-alloy catalysts, gasoline reforming, dehydrocyclisation by platinum alloys

1. Introduction

The platinum/alumina catalyst for gasoline reforming has been in use for over 40 years and has a complex chemistry. The reactions which it performs include dehydrogenation, C_5 ring opening, isomerisation and dehydrocyclisation. There is still dispute about mechanistic details, but it accepted that platinum is an unique metal in this context. There have been many surface science studies designed to probe its role in the reaction scheme and it was shown ca 20 years ago that platinum single crystal surfaces catalyse dehydrocyclisation of n-heptane to toluene, [1].

It is now universal practice to add another element to the reforming catalyst: a wide range of additives has been studied or proposed, of which rhenium has probably been the most successful commercially, [2]. Those which are known to the author are indicated in fig. 1, which also shows their location in the periodic classification. It can immediately be seen that the additives have no obviously common chemistry. They include metals from across the transition series, as well

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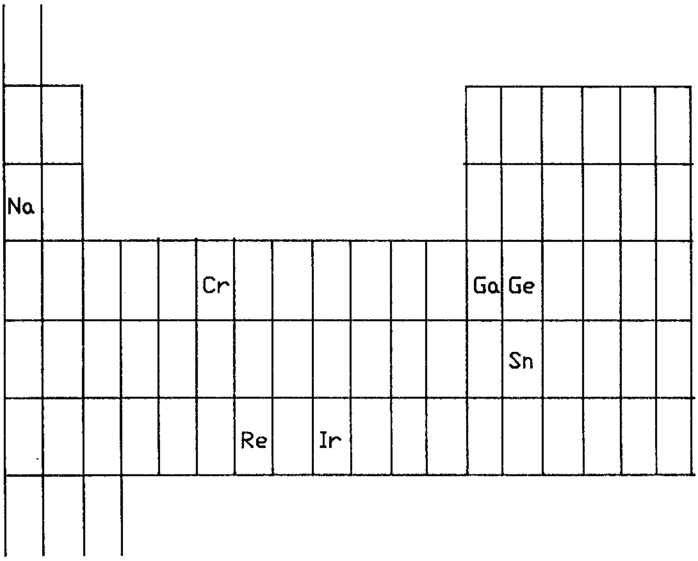

Fig. 1. Elements used or proposed as additives in platinum reforming catalysts.

as alkali metals, metalloid elements such as tin, and even the narrow band gap semiconductor germanium. The role of the additive is that of a gentle promoter of lifetime and yield. The mechanisms by which the additives function have been the subject of many studies, which it would be unfruitful to review here.

The purpose of this Letter is to propose a single explanation for the *modus operandi* for most of the additives. It is intended to exclude only the alkali metals, since it is clear that their effect is to increase dehydrocyclisation activity rather than to reduce coking, [3] and their use appears to require a special, non-acidic support. The model rests on evidence of three distinct types–the metallurgy of the bulk alloys formed between platinum and the additives: studies of the surface composition of some relevant materials using surface science techniques; and recent in situ studies of the composition of some Pt/Cr/H-ZSM-5 catalysts. The section that follows presents the evidence and the last part draws it together into a proposal.

2. The evidence

Our starting point is that the additive influences the behaviour of the platinum rather than the support. All of the additives can interact strongly with the metal, since alloy and ordered phases are known to exist, as summarised in table 1, [4]. Note that ordered phases are observed for four of the six elements of interest, and that, for the others, alloying occurs over most of the composition range. In the ordered phases there are interlocking lattices of platinum and the additive

Table 1
Alloys formed between platinum and elements used as additives to reforming catalysts.

Additive	Nature of alloy formed
Chromium	Alloy up to 78 at.% Cr, Ordered phase: Cr_3Pt, Superstructures at other compositions:
Gallium	Ordered phases: PtGa, Pt_2Ga_3, $PtGa_2$, Pt_3Ga_7:
Germanium	Ordered phases: Pt_2Ge, PtGe, Pt_2Ge_3:
Iridium	Alloy, complete miscibility, disputed evidence of ordering:
Rhenium	Alloy, two miscibility regions – < 42 at.% Re and > 58 at.% Re:
Tin	Alloy up to 8 at.% Sn, Ordered phases: Pt_3Sn, PtSn, Pt_2Sn_3, $PtSn_2$, $PtSn_4$.

element, so that each platinum atom exists in a well defined environment. Chromium is extensively soluble in platinum as well as forming an ordered phase. platinum and iridium are completely miscible and there is disputed evidence for an ordered phase. There is no indication of an ordered phase with rhenium, although the element does have significant solubility in platinum. The nature of the environment formed in a solid solution is not as well defined as that in an ordered phase, there is nevertheless likely to be a degree of ordering which will depend on the composition and the thermodynamics of the interaction.

Recent surface science studies have shown interesting and unexpected behaviour in the surface segregation properties of platinum alloys. At the level of a first approximation, surface segregation in vacuo is expected to be governed by surface energy, with the lower melting point component enriched in the outermost layer. Thus, in an alloy between platinum and a first row transition metal, platinum might be expected to segregate *away* from the surface, having a substantially higher melting point. Surprisingly, Gauthier et al. showed that, in a (111) single crystal of platinum and nickel, ($Pt_{78}Ni_{22}$), platinum is very substantially enriched and there is no detectable nickel in the surface monolayer, [5]. Similar observations have been made for platinum/titanium, [6], and for platinum/cobalt alloys, [7]. The precise factors responsible are not clear, but large differences in atomic diameter, (cp Pt, 2.78 Å: Ni, 2.49 Å) and strong intermetallic bonding are contributory factors.

These ordered platinum alloys have interesting and relevant chemisorption properties. For both $CoPt_3$ and Pt_3Ti surfaces the adsorption energy for carbon monoxide is substantially *lower* than on the equivalent pure platinum surface, [6,7]. This is unexpected, since both cobalt and titanium are able to adsorb carbon monoxide dissociatively, while only molecular chemisorption is observed for platinum.

The last piece of relevant evidence comes from our studies of chromium in Pt/H-ZSM-5 catalysts, using extended X-ray absorption fine structure, (EXAFS), [8,9]. Addition of chromium suppresses alkane hydrogenolysis when the catalysts are reduced at high temperature, ($T > 773$ K), although the effect is more marked for propane than ethane. EXAFS indicated that reduction at this high temperature causes the formation of small platinum/chromium alloy particles. These are 8–10 Å in diameter, with a total of 20–35 atoms per particle, of which 10–15% are chromium. X-ray photoelectron spectroscopy provides independent evidence of the presence of zerovalent chromium after high temperature reduction.

The ability of chromium to reduce hydrogenolysis activity is unexpected. There are no measurements of the hydrogenolysis activity of supported chromium catalysts, presumably because chromium is too difficult to maintain in the zerovalent state. Sinfelt's classic studies show that the hydrogenolysis activities of iron, cobalt and nickel, which might be expected to be similar to that of chromium, are about three orders of magnitude greater than that of platinum, [10]. It is therefore not obvious that adding chromium to a platinum surface should reduce hydrogenolysis activity. The situation is clearly different to that of adding copper to a ruthenium catalyst and we do not believe that it is reasonable to seek an explanation in terms of ensemble effects. Iridium and rhenium resemble chromium, since they are much more aggressive metals towards hydrocarbons than is platinum.

3. The model

Summarising the evidence, it is clear that the additives form ordered phases or alloys with platinum, that unexpected surface compositions can be observed for a number of the alloys of interest and that at least in some cases the additive element might be expected to *promote* rather than retard hydrogenolysis.

Making use of all of these observations, we propose that the surface monolayer of the active particle is platinum in all cases, and that the additive is not located in the outermost monolayer but in the immediate sub-surface layer, where its concentration will be enriched. The model is illustrated in fig. 2. The additive reduces hydrogenolysis by weakening the adsorption of hydrocarbons through an electronic interaction. It is known that platinum sits on the 'weak adsorption' side of the volcano curve for hydrogenolysis reactions, so that further weakening of hydrocarbon adsorption will reduce the rate of reaction. The sub-surface location of the additive explains why such a wide range of chemically disparate elements can be used effectively and without gross alteration of the catalyst chemistry.

The role of the additive is not well described by either the ensemble or the ligand concepts of Sachtler. It is clearly not appropriate to consider ensembles, since the active surface is entirely platinum. The ligand idea has more appeal, but is takes no account of the metallic nature of the active particles. An accurate description of the platinum/additive interaction must include the role of all of the atoms within the particle, perhaps through a consideration of the local

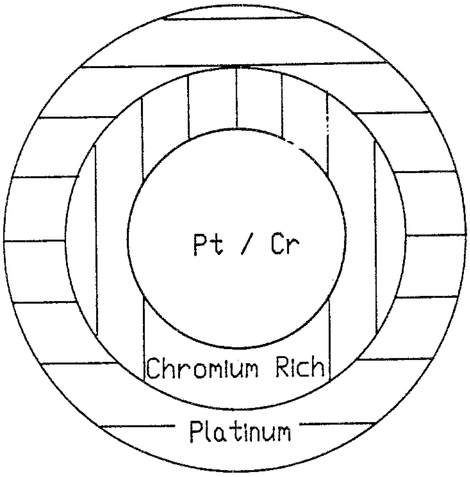

Fig. 2. The structural model proposed for alloying and surface segregation in platinum alloy reforming catalysts. The outer circles each represent one monolayer.

densities of states, [11]. New concepts are clearly needed to update the important Sachtler ideas and we believe that the *embedded surface molecule approach*, to be described elsewhere, [12], provides a suitable intellectual framework.

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References

[1] R.W. Joyner, B. Lang and G.A. Somorjai, J. Catal. 27 (1972) 405.
[2] H.G. Kluksdahl, USP 3,415,737.
[3] T. Edmonds and J.J. McCarroll, in: *Topics in Surface Chemistry*, Eds. E. Kay and P.S. Bagus (Plenum, New York, 1978) pp 261.
[4] M. Hansen, *Constitution of Binary Alloys*, 2nd Ed. (McGraw-Hill, New York, 1958).
[5] Y. Gauthier, Y. Joly, R. Baudoing and J. Rundgren, Phys. Rev. B 35 (1987) 6216.
[6] U. Bardi, D. Dahlgran and P.N. Ross, J. Catal. 100 (1986) 196.
[7] U. Bardi, B.C. Beard and P.N. Ross, J. Catal. 124 (1990) 22.
[8] R.W. Joyner, K.M. Minachev, P.D.A. Pudney, E.S. Shpiro and G. Tuleouva, Catal. Lett. 5 (1990) 257.
[9] P. Johnston, R.W. Joyner and E.S. Shpiro, to be published.
[10] J.H. Sinfelt, Catal. Rev. Sci. Eng. 3 (1976) 175.
[11] J.M. MacLaren, J.B. Pendry, R.W. Joyner and P. Meehan, Surf. Sci. 178 (1986) 856.
[12] R.W. Joyner, in: *Proc. 2nd Anglo-Dutch Conf. on Catalysis*, to be published in Catalysis Today.