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Organic Molecular Probes in Heterogeneous Catalysis. Hydrogenation of Norbornadiene on Gold

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Abstract A few important examples are described to show that well-chosen molecular probes in organic reactions on heterogeneous catalysts can reveal much about the nature of the active sites and reaction mechanisms. This approach using norbornadiene in hydrogenation casts much light on the reasons why highly dispersed gold is an active selective catalyst. In the new polar mechanism, H_2 undergoes heterolytic fission in the very act of addition to adsorbed alkene, in contrast to the conventional Horiuti-Polanyi mechanism based on prior homolytic dissociation of H_2 on the metal surface.

Keywords Organic probes · Selective hydrogenation · Polar mechanism · Gold catalysts · $Pt/ZrO_2/TiO_2$ · SMSI state

1 Introduction

The molecular organic probe approach to heterogeneous catalysis can be very effective especially when site densities are very low [1]. The correspondence between the homogeneous and heterogeneous fields can also be established, but so far this approach has not been widely appreciated. The fundamental requirement is the choice of a sufficiently complex substrate so as to contain the required specific chemical information in its structure in order to ask clear-cut questions about the nature of the active sites, the chemisorbed intermediates, and detailed reaction pathways.

Two important examples will serve as illustrations:

(1) Brönsted sites are essential in many reactions on highly acidic oxide catalysts such as activated silica–alumina and molecular sieves. The very low density of sites with high acid strengths (10^{10}–10^{12} $cm^{-2)}$ can be readily detected using the indicator and reactant.
1,1-diphenylethylene ($Ph_2C{=}CH_{2)}$ in non-polar solvents [1]. The results can be compared to those obtained from the addition of the same substrate at room temperature to conc. H_2SO_4/glacial acetic acid solutions of various acidic strength.
The first intermediate formed in both cases is the bright yellow carbenium ion Ph_2C^+–CH_3 (λ_{max}, 420 nm) which then reacts with $Ph_2C{=}CH_2$ itself thereby affording 1,1,3-triphenyl-3-methylindane and 1,1,3,3 -tetraphenyl-3-methylpropene respectively as the main products.
Both liquid and solid acids are also characterised by the slower formation of a bright blue more stable carbenium ion ($\lambda_{max,}$ 605 nm) formed by a tiny amount of dimerization via the less stable canonical form of the initial Ph_2C^+–CH_3 ion, as shown in Scheme 1.
The removal of the H^- ion from the unusual dimer by Lewis acidity, or by O_2 in the presence of Brönsted acidity, is extremely easy, and the product is the blue highly conjugated stable ion ($\lambda_{max,}$ 605 nm). The 1,1,3,3-tetraphenyl-3-methylpropyl carbenium ion cyclises on the solid acid to give the corresponding indane, but the reaction sequence is preferentially terminated in the liquid acids by precipitation of the methylpropene dimer.
It is worth noting that the most abundant chemisorbed species, the blue carbenium ion, is the least important

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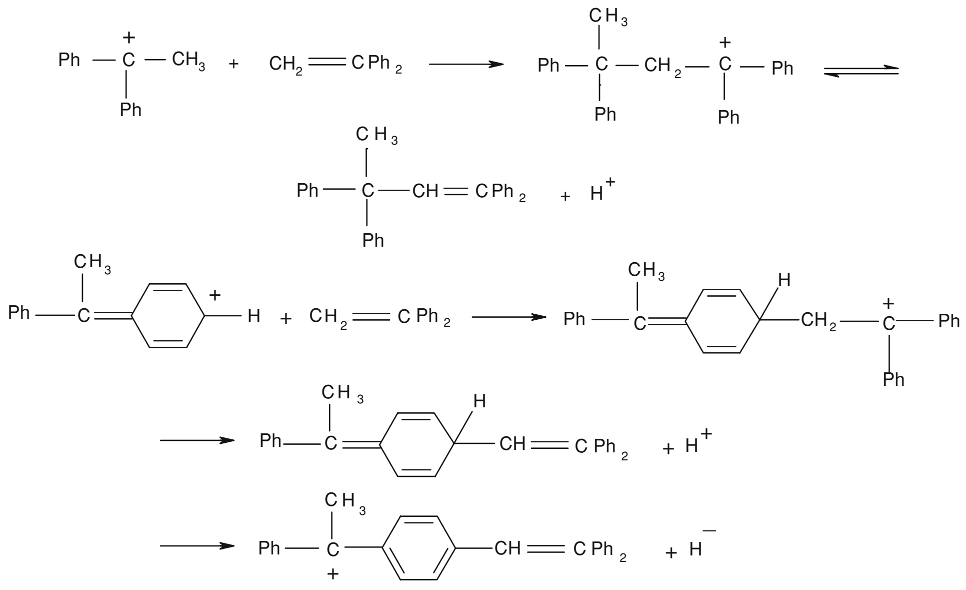
Scheme 1



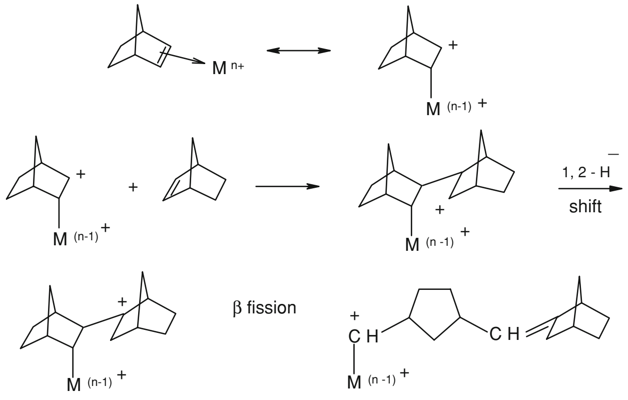
in the overall catalysis. This is often not generally appreciated in relating chemisorption to catalysis, and moreover emphasizes the value of the organic probe approach.

(2) The mechanism of olefin metathesis is now well established as the [2 + 2] metallacyclobutanation of a metallacarbene and an olefin, followed by orthogonal cleavage to give a new metallacarbene and a new olefin. The overall reaction proceeds via a chain mechanism, and the chain carrier is the metallacarbene. What is not immediately obvious is the mechanism of formation of the first metallacarbene in a variety of corresponding homogeneous and heterogeneous systems.

The ring-opening polymerisation of norbornene has been found to be a most valuable test [2]. Here, the ionic canonical form of the initial metal ion—norbornene complex is the key species. The norbornyl carbenium ion is known to be relatively stable. Once formed, it adds to a second norbornene molecule, so this step is exactly analogous to the first step in Scheme 1.

The metallacyclopentane intermediate is a zwitterion which contracts to the corresponding metallacyclobutane species via the favourable 1,2-H^- ion shift step. This is followed by the β fission of the C–C bond in the ionic form of the product metallacyclobutane to give the first metallacarbene, shown also in the ionic canonical form (Scheme 2).

The first aim of this preamble is therefore to show that ionic intermediates are often important in catalysis and that this is frequently not immediately obvious, as in metathesis polymerisation of norbornene. The second aim is to draw attention to the propensity of the bicyclo [2,2,1]-heptyl structure to adopt ionic forms. This will now be shown to be the underlying reason why norbornadiene has been found to be an extremely valuable probe for selective hydrogenation catalysis. The substrate has also the advantage that it is very cheap and readily available. As for the products, they are readily identified and analysed.



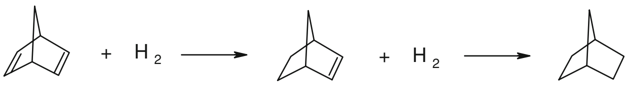
Scheme 2 n may equal zero

1.1 Metal Catalysts

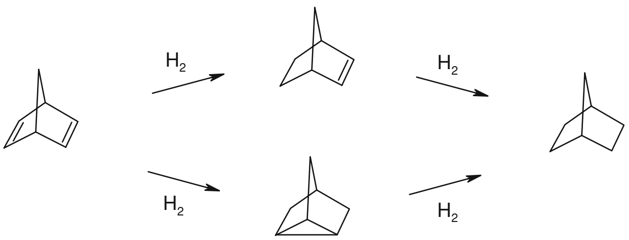
Active metal catalysts often consist of nano and even subnano metal clusters highly dispersed on refractory oxide supports. Here, the identification of the active sites, their number, and the reaction steps involved in the surface reactions, are much more formidable problems than in acid catalysis. The active site could consist of an ensemble of contiguous metal atoms as part of a regular crystal face. Alternatively, it could be an individual “defect” atom subtended by a crystal face and only present in very low

$$CH_3CH{=}CHCHO + H_2 \longrightarrow CH_3CH{=}CHCH_2OH$$
$$CH_2{=}CHC_6H_4NO_2 + H_2 \longrightarrow CH_2{=}CHC_6H_4NH_2$$

Scheme 3



Scheme 4



Scheme 5

numbers. The "defect" atoms could also be present in the oxide—metal crystal interface, and even in extreme cases as isolated individual metal atoms or ions embedded in the refractory oxide matrix.

These questions become really acute in the light of the recently noted remarkable reactivity and selectivity of extremely highly dispersed gold catalysts [3]. Two very recent and important papers [4, 5] examine in detail the various factors determining the high activity for CO oxidation on nano sized Au clusters on various supports. The catalytic activity of this metal came as a surprise because gold is not noted for the chemisorption of H_2, O_2, or CO. Yet, it has been shown to be quite active for CO oxidation [6] as well as being highly selective in hydrogenation. Thus the polar groups in crotonaldehyde [7] and in 3-vinylnitrobenzene [8] can be hydrogenated to give the corresponding $-CH_2OH$ and $-NH_2$ functionalities, leaving the propenyl, vinyl, and phenylene groups largely intact (Scheme 3).

2 Results and Discussion

2.1 Hydrogenation of Norbornadiene

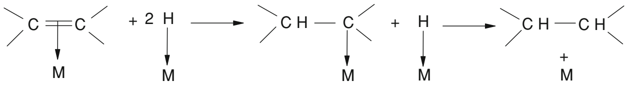
We report here that hydrogenation of norbornadiene is a very valuable probe for the study of gold catalysts and other metals with comparable catalytic activity and selectivity. When this substrate is passed in H_2 over a standard Pt/SiO_2 catalyst (323–373 K), the only products are norbornene and norbornane (Scheme 4). A standard Pt/SiO_2 catalyst is one that has been tested by the cyclopentane/D_2 exchange reaction [9] at room temperature, showing high activity, with the initial distributions of deuteroisomers characteristic of Pt metal, including Pt films.

However, when the same reaction is carried out using a Au/SiO_2 catalyst (2 wt% metal) prepared by impregnation method using $HAuCl_4$ acid solution, the products also contain nortricylene [10] (Scheme 5). Nortricyclene was present in much the same amount as the other intermediate product, its norbornene isomer, throughout the course of the reaction.

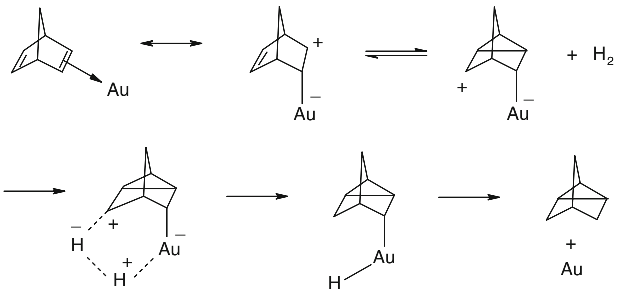
The presence of nortricyclene is very revealing about the reaction mechanism and the nature of the active sites. In conventional hydrogenation, as on Pt, the adsorbed alkene is supposed to react according to the Horiuti-Polanyi mechanism with chemisorbed H atoms formed by prior homolytic dissociation of H_2 molecules (Scheme 6).

However, the presence of nortricyclene (thermodynamically about three times more stable than norbornene up to 373 K) in the products clearly reveals that the hydrogenation is now due to a polar mechanism (Scheme 7).

The H_2 molecule now undergoes heterolytic fission in the very act of addition to the substrate in contrast to the Horiuti-Polanyi mechanism of prior homolytic dissociation. Thus, the active site in Au catalysts, which do not chemisorb H_2 in a fashion similar to that of Pt, could well be an individual or isolated electron-deficient Au atom, perhaps even an ion. The new mechanism in Scheme 7 with the emphasis on ionic intermediates shows why Au catalysts selectively hydrogenate polar functionalities [7, 8]. There is also a striking parallel to homogeneous catalysis by Au and the role of ionic intermediates [3]. Furthermore, details of the i.r. spectroscopic analyses of the photocatalytic hydrogenation of norbornadiene by group 6 metal carbonyls [11] support all these conclusions. Non-classical dihydrogen complexes,



Scheme 6



Scheme 7

(η^4—norbornadiene) $M(CO)_3$ (η^2–H_2), were detected and nortricyclene was found amongst the reaction products.

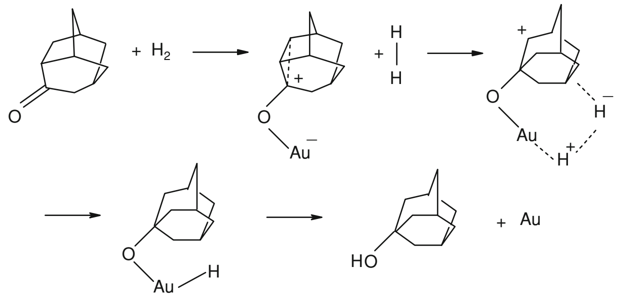
The formation of nortricyclene in this homogeneous reaction is powerful evidence that when it is found in norbornadiene hydrogenation on supported metals, the active centre is also an individual electron-deficient metal atom or even metal ion, which holds simultaneously both the substrate molecule and the H_2 molecule as transient ligands. The organic probe is therefore diagnosing the presence and importance of these active centres. This is our primary concern rather than the size distribution of the metal particles. Moreover, recent work [4, 5] shows clearly that nanoparticles of Au are the most active in catalysis, and this is consistent with the theory that electron-deficient atoms are important in the polar mechanism.

The norbornadiene hydrogenation test is recommended also for other metal catalysts which behave like gold. Of particular interest is $Pt/ZrO_2/TiO_2$ in the SMSI state which does not chemisorb H_2 [12], but exhibits selective hydrogenation of crotonaldehyde [13] similar to that described for Au [7].

2.2 Hydrogenation of Protoadamantanone

The isomerisation of protoadamantane to adamantane is highly exothermic ($\Delta H \approx 36$ kJ mol^{-1}) so the protoadamantyl carbenium ion rearranges very rapidly via a 1,2-bond shift step to give the isomeric adamantyl ion. This knowledge has now been used as the basis for another good test for the role of polarity in the mechanisms of hydrogenation on Au, Pd, and Pt catalysts. Thus, protoadamantanone hydrogenates on Au at 373 K to give adamantanol. But using supported Pd and Pt, both highly active in dissociative adsorption of H_2, the products are protoadamantanol and protoadamantane. The mechanism for this hydrogenation on Au is shown in Scheme 8.

Heterolytic fission of H_2 with simultaneous addition to the polarized ketone—Au surface complex is clearly indicated by the adamantanol product. By way of contrast, the mechanism of hydrogenation of the ketone on highly active Pd and Pt, and of hydrogenolysis of the resulting protoadamantanol, is not sufficiently polar to induce the rearrangement of the intermediate protoadamantyl structure.



Scheme 8

The extension of the mechanism in Scheme 8 to selective hydrogenation of crotonaldehyde on Au is obvious. The homogeneous activation of H_2 by Au ions in solution also seems to occur via a heterolytic mechanism [3].

However, a Pt/SiO_2 catalyst made by accidentally heating SiO_2 impregnated with H_2 $PtCl_6$ to 673 K for 1 h prior to reduction in H_2 at that temperature was also found to rearrange the protoadamantyl skeleton of the intermediate in the protoadamantanone hydrogenation. Like Au, this particular Pt catalyst had no activity for exchange of adamantane with D_2, a reaction which proceeds rapidly at 293 K on normal Pd and Pt catalysts, which readily promote dissociative chemisorption of paraffins and H_2 via homolytic fission of C–H and H–H bonds. The conventional catalysts are made by reduction of H_2 $PtCl_6/SiO_2$ with H_2 at room temperature before being annealed in H_2 at elevated temperatures. The behaviour of the unusual Pt catalyst therefore resembled that of $Pt/ZrO_2/TiO_2$ catalysts [13] which are also prepared in the SMSI state by prolonged high temperature treatment in H_2.

The idea of polarity as a potential key feature in reactions involving chemisorbed substrates on metal was also put to good use in the following example. When quinoline is reacted with D_2O using a Pt/SiO_2 catalyst, there is nondiscriminate exchange of all the H atoms around the aromatic rings. A flat π-bonded orientation of the quinoline molecule during the surface reaction is obviously important so the reaction is non-selective.

Since selective exchange of the α-H on the carbon atom adjacent to the N atom in quinoline was desired, it was therefore suggested that the mechanism should be made polar by addition of NaCl to the D_2O solution. It was hoped that the presence of Cl^- ions on the Pt surface would change the orientation of the chemisorbed quinoline from flat-on to end-on, via dative bonding from the lone pair on the N atom to the electron-deficient sterically crowded Pt atom. This prediction worked well. The change from non selective to selective exchange was achieved by this modification of the catalyst system [Hardacre C, unpublished results] thus confirming our prediction, so it would be very interesting to check such modified metal catalysts using the norbornadiene test reaction in ethanolic solutions [10] where both substrate and salts will dissolve.

3 Conclusion

The general conclusion is that in the search for selective heterogeneous catalysts for organic conversions under mild conditions, potential and actual polarity of the reaction intermediates should be given serious consideration. A key factor then is to produce and maintain good densities of individual or even isolated electron-deficient metal atoms and ions on the catalyst surfaces.

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