Platinum-Carbon Catalysts with Molecular Sieve Properties

SHAPE SELECTIVITY IN HYDROGENATION CATALYSIS

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Applications of molecular sieve materials have become of increasing interest in catalysis. The ability of these materials to differentiate on the basis of molecular size gives them a unique form of selective catalytic action with the additional benefit of high resistance to sorption of large poison molecules. Hitherto their major application has been realised with zeolites but new platinum catalysts possessing similar properties and based on a carbonaceous structure have now been developed in the Johnson Matthey Research Laboratories.

Over the past few decades increasing interest has been aroused in the field of adsorption, and to a lesser extent catalysis, by materials which, as a result of their structure, are capable of selectively differentiating between molecules of differing size. These materials, often described as molecular sieves, contain an internal volume of pores whose width is commensurate with the cross-sectional diameter of such molecules as nitrogen, carbon dioxide, and the normal hydrocarbons, whereas branched hydrocarbons with tri- and tetra-alkyl substitution are too large to enable access to the internal pore structure to occur. Selective adsorption therefore results from steric hindrance to diffusion through the porous medium and is distinct from selective adsorption as a result of a specific chemical reaction.

The major application to date of molecular sieves has been realised with the application of zeolites (crystalline alumino-silicates) to such problems as gas and solvent purification (1). The inherent ability of zeolites to adsorb selectively molecules entering the pore structure renders them ideal for removing such impurities as water from damp gas streams, the purification of hydrocarbon solvents, and the separation of hydrocarbon mixtures. Such compounds also have the advantage that pore size may be tailored by altering the chemical composition of the zeolites, thereby altering the molecular sieve characteristics of the solid (2).

Another class of compounds which may show the existence of molecular sieve properties are the amorphous carbons, and recently interest in certain of these carbons has been revived by molecular sieve technology. Early evidence for the existence of molecular sieve properties in microporous carbons was presented by Franklin (3) who reported that the apparent density of carbons during graphitisation depended on the fluid immersion medium, larger molecules giving lower densities due to incomplete penetration of the pore structure. Bond and Spencer (4) have also deduced that a significant proportion of the surface area of coals was associated with pores of diameter less than 5 to 8Å.

Recent developments in this field have shown that a great number of coals, cokes and notably organic polymer chars are molecular

sieves. Unfortunately a major disadvantage of organic chars is the low adsorptive capacity which reduces their economic importance in relation to zeolites. This difficulty was overcome by the development of a composite carbon molecular sieve (5) which consists of a non-selective, high area activated charcoal coated with charred thermosetting polymer.

A significant difference between the zeolites and carbon molecular sieves (CMS) has been demonstrated by molecular probe adsorption studies (5). Thus by adsorbing both cylindrical and planar molecules of varying size, the zeolites were demonstrated to possess cylindrical pore mouths in accord with their crystalline structure, whereas CMS possessed slit pore geometry probably resulting from the formation of micro-fissures between turbostratic graphitic platelets in the carbon (6).

Molecular Sieves in Catalysis

Porous solids have long been employed as a means of efficiently distributing expensive catalytic constituents such as platinum and other precious metals. By such means the surface volume ratio of the catalytic metal may be maximised to ensure the fullest possible use of the metal in the catalytic reaction. Several other important advantages are often claimed for supported catalysts such as the inherent chemical superiority of the support-catalyst complex (7), and the dual role of both catalyst and 'support' that is obtained, for example, using platinum on acidic alumina for petroleum reforming (8).

On the other hand, the use of a porous support to distribute catalytic metal is not without its disadvantages. Not only can the chemical composition of the support influence the performance of the catalyst but its physical structure also. The various stages in a catalytic reaction at a solid surface are considered to be as follows:

    (i) diffusion of reactants to the active site;
    (ii) adsorption on to the catalyst, reaction and desorption of products;
    (iii) diffusion of products away from the catalyst.

Thus it is clear that when the active site is deposited within a porous structure, steps (i) and (iii) are of considerable importance as the reactants and products may have to negotiate long and tortuous paths to the active centre.

The transport of material through porous structures is dependent on pore size, and as pore size decreases a point may be reached where the rate of diffusion of reactants or products is slower than that of catalytic reaction, and the reaction becomes diffusion controlled (9). This condition is generally avoided by careful design of the catalyst as it represents an inefficient use of expensive metal not only in terms of decreased activity per unit weight of metal, but decreased selectivity also. At extremely small pore sizes the reactant may be totally prevented from entering the pore system because the molecular size of the reactant is larger than the pore entrance. Conversely, smaller molecules will continue to diffuse into and out of the pore system. If a catalytic site is present within such a pore system a unique form of catalytic selectivity will be obtained where the molecular sieve effect of the support dictates the size of molecule which reacts.

Molecular sieve catalysts have been realised in practise by the use of zeolites which are both catalysts in their own right (10), and also used as supports for active material (11, 12). Such catalysts are highly selective in both cracking reactions and hydrogenation reactions, selective cracking of n-paraffins in a mixture of n- and iso-paraffins occurring over the zeolite alone, and selective hydrogenation of n-alkenes in the presence of branched alkenes occurring over a platinum-impregnated zeolite. The latter catalyst also showed high resistance to large poison molecules (12) such as thiophen, purely as a result of the molecular sieve structure dictating the size of molecule capable of reaching active sites.

Carbon Molecular Sieve Catalysts

Until quite recently (13) no reports have appeared in the literature of the use of carbon

molecular sieves as catalyst supports, although innumerable advantages of carbonaceous materials are claimed in comparison to zeolites (14). Of these the main claims are the cheapness of preparation, the thermal stability, and their resistance to attack by strong acid or alkali.

Perhaps the lack of interest shown has been as a result of the difficulty of impregnating carbon molecular sieves with active catalyst and subsequently maintaining selectivity. In the zeolitic system impregnation is relatively easy and consists simply of ion-exchanging the zeolitic cation for that of the catalytic metal, salt, followed by reduction. As a result the cations are situated at the centre of the "cage-like" crystal structure and thus the catalyst material is embedded within the molecular sieve framework. Carbon molecular sieves, however, are highly amorphous, and although there are probably functional groups available for the attachment of metal salts a high proportion would exist on external surface. Obviously, catalytic stereo-selectivity due to the molecular filter action of the support would be lost if metal is deposited on surface, external to micropores.

Work in the Johnson Matthey Research Laboratories has led to several novel methods of preparation of carbon molecular sieve catalysts. The aim of the work has been to disperse an active catalytic metal (e.g. platinum) throughout a molecular sieve framework such that the metal is embedded within the microporous structure of the sieve. Under these conditions the ability of reactant molecules to diffuse through the molecular sieve automatically selects the size of reacting molecule. As conventional methods of preparation such as impregnation of charcoal with a metal salt from solution are unsuitable, the reverse procedure has been adopted

Table I
The Hydrogenation of Linear and of Branched Olefins over Conventional Platinum/Charcoal and over Platinum/Carbon Molecular Sieves

A 1.78×10^{-4} moles/pulse at 25°C. Reciprocal space velocity 9.0×10^{-3} g.min/cm³			B 2.00×10^{-4} moles/pulse at 30°C. Reciprocal space velocity 4.0×10^{-4} g.min/cm³		
Olefin	Alkane produced (mole $\times 10^4$)		Olefin	Alkane produced (mole $\times 10^4$)	
	Pt/CMS 1	10% Pt/C		Pt/CMS 2	2% Pt/C
a propylene	0.165	1.49	b butene-1	0.22	1.77
b butene-1	0.06	1.28	c isobutene	0.02	1.14
c isobutene	0	1.32	e 3,3-dimethyl-butene-1	0.02	0.99
d 3-methylbutene-1	0	1.25			
Selectivity $\dfrac{a}{a+c}$	1.0	0.53	Selectivity $\dfrac{b}{b+c}$	0.92	0.61
Selectivity $\dfrac{b}{b+d}$	1.0	0.51	Selectivity $\dfrac{b}{b+e}$	0.92	0.64

a propylene;   b butene-1;   c isobutene;   d 3-methyl-butene-1;   e 3,3-dimethyl-butene-1

$$C-C=C \qquad C-C-C=C \qquad \begin{matrix} C \\ | \\ C-C=C \end{matrix} \qquad \begin{matrix} C \\ | \\ C-C-C=C \end{matrix} \qquad \begin{matrix} C \\ | \\ C-C-C=C \\ | \\ C \end{matrix}$$
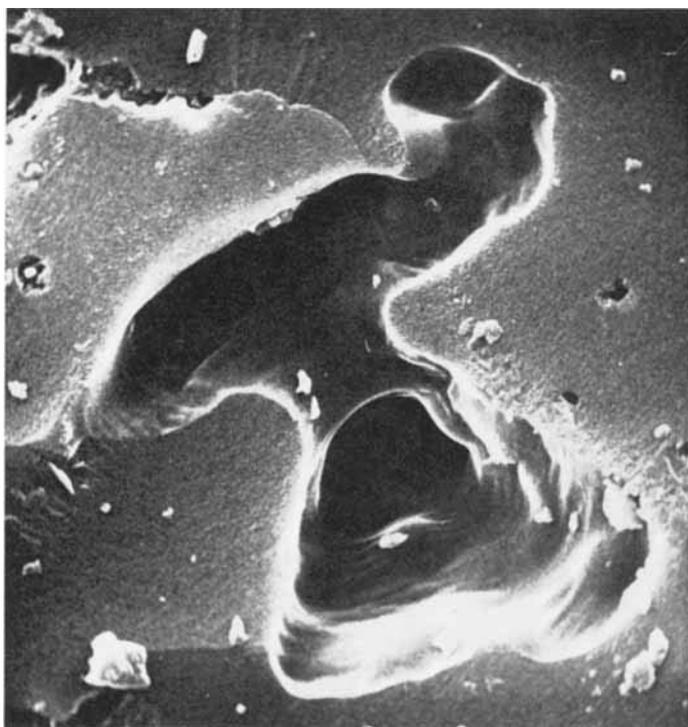
whereby the carbonaceous structure is developed around a platinum dispersion in solution. In essence the process involves the polymerisation of an alcoholic medium containing a colloidal suspension of platinum. A thermosetting resin is obtained which is carbonised under oxygen-free nitrogen to form the platinum/CMS catalyst (Pt/CMS 1 in Table I). A second method has also proved highly satisfactory, and is in fact a variation on the composite carbon molecular sieve preparation (5). In this case a conventional platinum/charcoal catalyst is coated with thermosetting polymer and carbonised, with the result that a molecular sieve skin is formed over the original catalyst (Pt/CMS 2 in Table I). This type of preparation has the obvious advantage that it may be extended to any form of solid catalyst.

Studies (13) have shown these materials to be highly selective adsorbents capable of differentiating between linear and branched hydrocarbons, with the result that only linear molecules are capable of penetrating to the internal pore structure. Thus a typical material was found to adsorb nitrogen and butane, but not isobutane and neopentane, the adsorptive capacity towards the former gases (expressed for convenience in terms of surface area) being 100 m^2/g and 20 m^2/g.

Scanning electron microscopy (see Figure 1) was only capable of detecting extremely large pores 0.5 to 3 microns diameter, the rest of the material appearing quite homogeneous. No surface platinum was detected by this method.

Catalytic Selectivity

The catalysts were tested for hydrogenation activity using linear and branched mono-olefins as reactants. The olefins chosen were propylene, butene-1, isobutene, 3-methyl-butene-1, and 3,3-dimethylbutene-1. These were chosen to show how catalytic behaviour varies with their molecular structure. As can be seen from the carbon skeletons in Table I, the effective molecular diameter increases as more branching occurs.

The reaction was studied using a pulse flow micro-reactor attached to a gas chromatographic analyser. A study of the elution of reaction products from the hydrogenation of propylene using the pulsed flow technique rapidly established the slow diffusion of reaction product from the catalyst. It can be seen (Fig. 2) that the propane concentration continues to increase long after the propylene concentration reaches a maximum (i.e. when the reactant pulse has passed the catalyst). Such an effect is almost certainly associated with the slow diffusion of product from the molecular sieve support.

The stereoselectivity of the catalysts for mono-olefin hydrogenation is shown in Table 1 where selectivity is expressed as:

$$\frac{\text{linear olefin produced}}{\text{linear olefin} + \text{branched olefin produced}}$$

Thus selectivity may vary from 1.0, where only linear olefin reacts, to 0.5 where both linear and branched olefins react at equal rates. From a comparison of molecular sieve catalysts with conventional Johnson Matthey platinum on charcoal catalysts it is apparent that the molecular sieve catalysts are highly

shape selective. It is interesting to note that whereas the conventional catalyst displays a small degree of selectivity that may be associated with decreasing activity with increasing methyl substitution about the olefinic double bond, the high selectivity of the molecular sieve catalyst is almost certainly associated with limitation of access to active sites by molecular size.

Certain preparations of platinum-containing CMS catalysts, however, showed lower selectivity than others (Table II). This was found to be associated with the presence of surface metal as demonstrated by the results on the uncarbonised polymer which has no pore structure. Two methods of inducing high selectivity on these catalysts have been developed based on a form of selective poisoning. The first method consists simply of recoating the catalyst with another layer of molecular sieve. The second method consists of poisoning the metal accessible to larger molecules using a poison of similar size. Both methods are successful in inducing high selectivity (Table II). To reduce the hydrogenation of 3,3-dimethylbutene-1 the
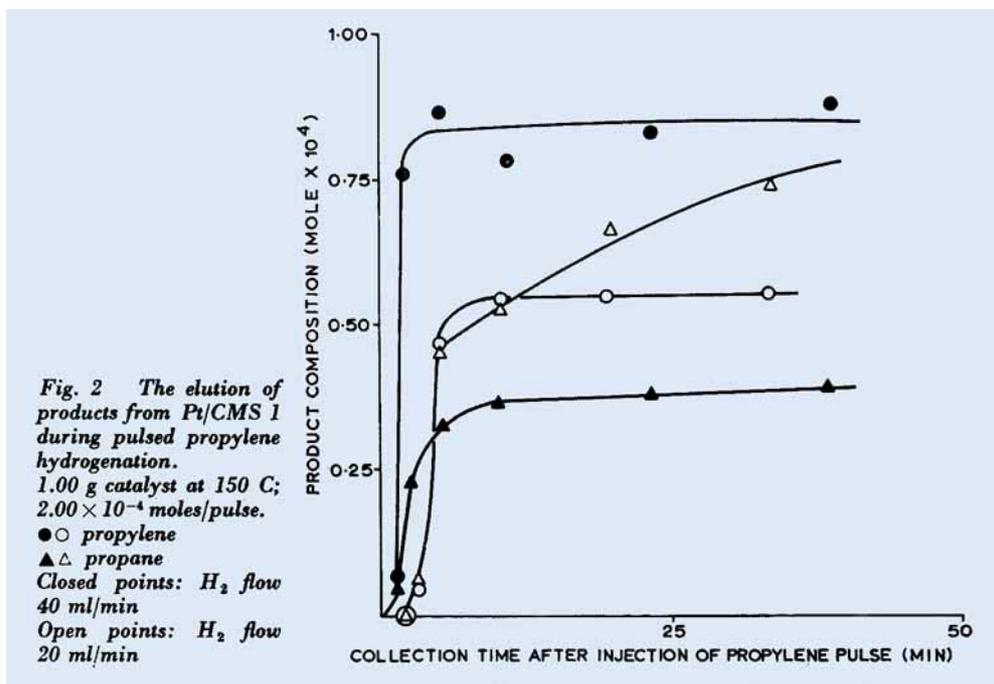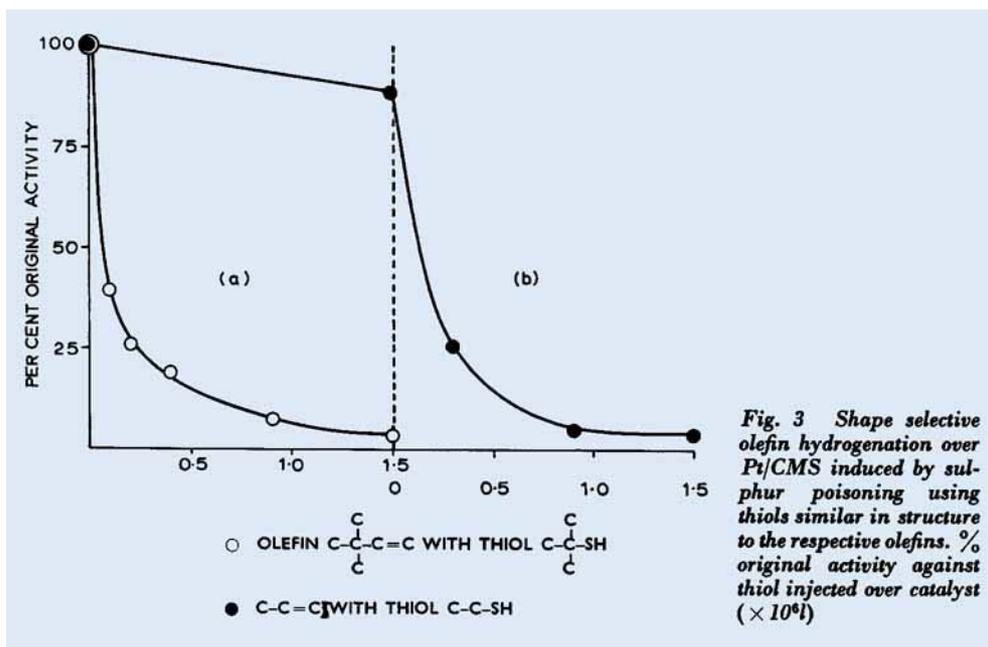

Fig. 2 *The elution of products from Pt/CMS 1 during pulsed propylene hydrogenation.*
1.00 g catalyst at 150 C;
2.00 × 10⁻⁴ moles/pulse.
● ○ *propylene*
▲ △ *propane*
Closed points: H₂ flow 40 ml/min
Open points: H₂ flow 20 ml/min

Table II

The Selectivity of Poisoned Pt CMS Catalysts in Mono-olefin Hydrogenation

A   Poisoning by recoating with carbon molecular sieve. The hydrogenation of (*a*) propylene and of (*b*) isobutene at 150°C. 2.00×10^{-4} moles/pulse.   Reciprocal space velocity 0.040 g.min. cc.$^{-1}$

Catalyst	Propane produced (mole × 10^4)	Isobutane produced (mole × 10^4)	Selectivity
Uncoated polymer	1.35	0.37	0.78
Uncoated catalyst	1.30	0.52	0.71
Coated polymer	0.17	0.09	0.65
Coated catalyst	0.45	0.02	0.96

B   Poisoning by injection of 1.5×10^{-6}l. 2-methyl-2-propane thiol. The hydrogenation of propylene and of 3,3-dimethyl-butene-1 at 150°C. 2.00×10^{-4} moles/pulse.   Reciprocal space velocity, 0.021 g.min.cc^{-1}

Catalyst	Propane produced (mole × 10^4)	2,2-dimethylbutane produced (mole × 10^4)	Selectivity
Before poisoning	2.00	1.50	0.57
After poisoning	1.76	0.02	0.99

catalyst was poisoned with 2-methyl-2-propane thiol, $(CH_3)_3CSH$, (Fig. 3a) the activity towards propylene hydrogenation remaining virtually unchanged. However, on injecting ethane thiol, CH_3CH_2SH, (Fig. 3b) the propylene activity rapidly decayed because the smaller poison molecule was capable of reaching the active sites for propylene

Fig. 3   Shape selective olefin hydrogenation over Pt/CMS induced by sulphur poisoning using thiols similar in structure to the respective olefins. % original activity against thiol injected over catalyst ($\times 10^6 l$)

hydrogenation existing within the molecular sieve structure. Both poisoning curves are typical of those found with pore mouth poisoning (15), but are unique in demonstrating the high resistance of the catalyst to large poison molecules.

These novel Johnson Matthey catalysts, therefore, are both highly selective in their catalytic action and highly resistant to large poison molecules. They would therefore appear to be comparable to zeolitic systems, which are finding a growing number of commercial applications. They do possess several advantages over zeolites both in the inherent advantages of the use of a carbonaceous support outlined previously, and also they are easily adapted for use as a composite catalyst with any solid catalytic material. They also offer several interesting possibilities in that the composite preparation offers a potential method for more precise control of the commercial activated carbons commonly used as catalyst supports.

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References

1 "Union Carbide Molecular Sieves for Selective Adsorption", British Drug Houses Ltd, Poole, England

2 R. M. Barrer, *Nature*, 1955, **176**, 1188

3 R. E. Franklin, *Trans. Faraday Soc.*, 1949, **45**, 668

4 R. L. Bond and D. H. T. Spencer, "Industrial Carbon and Graphite", Soc. Chem. Ind, 1958, 231

5 P. L. Walker, T. G. Lamond and J. E. Metcalfe, 2nd Int. Carbon & Graphite Conference (S.C.I.), London, 1965

6 W. F. Wolff, *J. Phys. Chem.*, 1958, **62**, 829

7 A. C. C. Tseung and B. S. Hobbs, *Platinum Metals Rev.*, 1969, **13**, (4), 146

8 V. Haensel and H. S. Bloch, *Platinum Metals Rev.*, 1964, **8**, 2

9 A. Wheeler, *Advances in Catalysis*, 1951, **3**, 250

10 P. B. Weisz, V. J. Frillette, R. W. Maatman and E. B. Mower, *J. Catalysis*, 1962, **1**, 307

11 J. A. Rabo, P. E. Pickert, D. N. Stamires and J. E. Boyle, *Actes du Deuxieme Congrès Internationale de Catalyse*, 1960, **2**, 2055.

12 J. A. Rabo, V. Shoemaker and P. E. Pickert, *3rd. Int. Congress on Catalysis*, 1964, **2**, 1264

13 B. J. Cooper and D. L. Trimm, paper to be presented at the 3rd Int. Carbon & Graphite Conference (S.C.I.), London, 1970

14 D. H. T. Spencer, "Porous Carbon Solids", Ed. R. L. Bond, Academic Press, London and New York, 1967, 87

15 P. G. Ashmore, "Catalysis and Inhibition of Chemical Reactions", Butterworths, London, 1963, 190

Platinum Metal Coatings for Stereoscan Specimens

The Stereoscan electron microprobe system produced by Cambridge Instruments Limited eliminates much time-consuming specimen preparation work associated with, for example, transmission electron microscopy. Specimen preparation generally involves only drying, fixing on to the specimen stub and rendering the specimen conductive by evaporating a metal layer, e.g. 300 to 500 Å gold-palladium alloy, on to it to prevent charge formation without masking the surface detail and impairing resolution.

Workers at the London School of Hygiene and Tropical Medicine, under the direction of Professor A. W. Woodruff, have now used rhodium vapour in this way to obtain excellent Stereoscan pictures of the surface of Toxocara canis larvae, which occur in the intestines of dogs. Larvae which arise in man from the eggs of Toxocara canis burrow into the human intestine wall and are carried by the bloodstream to organs such as the eye, where damage may occur. They also predispose man to virus infections such as poliomyelitis.