The Preparation of Selective Carbon Molecular Sieve Catalysts

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Summary Carbon molecular sieve catalysts have been prepared which show shape selectivity for olefin hydrogenation.

RECENT studies[1,2] have shown that it is possible to prepare carbons of well defined pore characteristics by the carbonisation of polymerised furfuryl alcohol. These carbons, which contain slit pores between 4 and 6 Å wide, are referred to as carbon molecular sieves (CMS) because of their ability to adsorb varying amounts of gas as a function of molecular size. We report the preparation and characterisation of selective catalysts obtained by combination of a metal with CMS supports.

In order to maintain selectivity it is necessary to disperse the metal within the pore structure of the carbon. Two main methods have been found suitable. In the first, a mixture of furfuryl alcohol, platinum oxide, and formaldehyde was warmed to 40° and further formaldehyde was added to ensure the reduction of the oxide. The platinum produced was suspended in solution as a colloid. The solution was warmed to 90° and a solution of phosphoric acid was added to initiate polymerisation of the alcohol. The polymer was cured at 110° for 6 hr., and then at 200° for 6 hr. The deposit was then crushed (< 2 mm) and carbonised at 600° for 4 hr. (Pt/CMS I).

The hydrogenation of linear and of branched mono-olefins over platinum–charcoal and platinum–carbon molecular sieve catalysts

Pt/CMS I: 1·00 g. $1{\cdot}78 \times 10^{-4}$ moles/pulse at 25°. Reciprocal space velocity $9{\cdot}0 \times 10^{-3}$ g. min. cm^{-3}.

Pt/CMS II: and 2% Pt/C 0·05 g. $2{\cdot}00 \times 10^{-4}$ moles/pulse at 30°. Reciprocal space velocity $4{\cdot}0 \times 10^{-4}$ g. min. cm^{-3}.

	Alkane produced (mole $\times 10^4$)		
Alkene	Pt/CMS I	Pt/CMS II	2% Pt/C
(a) Propene	0·17	—	—
(b) But-1-ene	0·06	0·22	1·77
(c) Isobutene	0	0·02	1·14
(d) 3-Methylbut-1-ene	0	—	1·33
(e) 3,3-Dimethylbut-1-ene	—	0·02	0·99

Selectivity	Pt/CMS I	Pt/CMS II	2% Pt/C
a/(a + c)	1·0	—	—
b/(b + c)	1·0	0·92	0·61
b/(b + d)	1·0	—	0·57
b/(b + e)	—	0·92	0·64

In the second preparation, a liquid polymeric resin was prepared as above, but in the absence of platinum. A conventional supported catalyst was then immersed in the resin, removed, and drained at 90°. In the present studies, a 2% Pt on charcoal catalyst, kindly provided by Johnson Matthey and Co. Ltd., was used as a base, but any catalyst of suitable structure may be used. The composite coated sample was then cured and carbonised as described above. (Pt/CMS II).

The shape selectivity of Pt/CMS in hydrogenation catalysis was examined by pulsing linear and branched mono-olefins through a bed of catalyst using hydrogen as the carrier. Preferential hydrogenation of the smaller linear olefins was demonstrated by expressing the selectivity of the catalyst as,

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

such that a selectivity of 1·0 represents linear olefin hydrogenation only. Thus both Pt/CMS I and Pt/CMS II clearly show shape selectivity for olefin hydrogenation, whereas the conventional platinum–charcoal catalyst is virtually unselective.

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[1] P. L. Walker, jun., T. E. Lamond, and J. E. Metcalfe, tert., 2nd Industrial Carbon and Graphite Conference, (S.C.I.) London, 1965.

[2] B. J. Cooper and D. L. Trimm, paper to be presented at the 3rd Industrial Carbon and Graphite Conference (S.C.I.), London, 1970.