

# Ruthenium and Osmium as Hydrogenation Catalysts

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*Little attention has been given to the use of ruthenium and osmium as catalysts for vapour-phase reactions. This paper shows that both these metals when supported on alumina possess significant activity for the hydrogenation of unsaturated hydrocarbons. In the hydrogenation of butene, butadiene and acetylene their activity is comparable with that shown by the other platinum group metals, although ruthenium is generally more active than osmium.*

Although much attention has been paid in recent years to the use of Group VIII metals as hydrogenation catalysts, comparatively little work has been done with ruthenium and even less with osmium.

As early as 1925, Fischer and Tropsch (1) found that the order of activity of the Group VIII metals for the formation of methane from carbon monoxide and hydrogen was



and later Pichler (2) discovered that, at high pressures and temperatures, the Fischer-Tropsch synthesis yielded high molecular-weight paraffins when ruthenium was used as catalyst.

Most of the literature deals with the catalytic properties of ruthenium and osmium in the liquid phase. Supported ruthenium catalysts are specific for the hydrogenation of carbonyl groups and will preferentially reduce carbonyl groups in the presence of ethylenic linkages (3). Recent work by Rylander *et al.* (4) has shown that most of these reductions are not possible unless water is used as solvent. Ruthenium will reduce sugars (3), and, at high temperatures and pressures, polysaccharides (5), to polyhydroxy alcohols.

Ruthenium alone is completely inactive for the hydrogenation of nitro groups, although under suitable conditions it will readily reduce

oximes and hydroxylamines to the corresponding amines (6). When mixed with either palladium or platinum, ruthenium displays a synergistic effect, the mixed catalysts showing greater activity for the reduction of both aliphatic and aromatic nitro compounds, ketones, pyridine, nitriles and butyne-diol than either metal alone.

Sheridan and Reid (7) found that both ruthenium and osmium possessed very little activity for the vapour phase hydrogenation of acetylene and Sokol'skii (8) found that, in alcoholic solution, ruthenium was completely inactive for the hydrogenation of acetylenic compounds, although when mixed with platinum or palladium both ruthenium and osmium promoted the hydrogenation of ethylenic compounds. Acetylenes are non-selectively reduced by ruthenium (9). Ruthenium in the liquid phase is claimed (9) to exhibit a high selectivity for the hydrogenation of mono-substituted olefins in mixtures of olefins, because the rate of double-bond migration is less than the rate of hydrogenation. It is also claimed (9) that ruthenium shows little tendency to promote cis-trans isomerisation. Ruthenium is also active for the hydrogenation of aromatic molecules (10).

The catalysts studied in the course of the present investigation consisted of 1 per cent

metal supported on  $\alpha$ -alumina and were prepared by evaporation of a solution of a salt of the metal on to the support. Ruthenium trichloride and ammonium chlorosmate were the salts chosen since both are water soluble. However, it was soon found that when an aqueous solution of either salt was heated, the salt decomposed with the formation of a black precipitate. Since acids attack the support, acidic solutions could not be used, although they were stable to heat. In 2N ammonium hydroxide solution, the ruthenium trichloride does not decompose and the ammonium chlorosmate decomposes to an appreciably smaller extent than in aqueous solution. To overcome the decomposition of the osmium salt, the excess water was removed, after the impregnation of the support, by evaporation under reduced pressure at room temperature. This method proved unsatisfactory, however, since in the resulting catalyst, the metal was very unevenly distributed on the support. It was finally decided to use an alkaline solution of

**Table I**

**Kinetics of Hydrogenation Reactions over Ruthenium**

Hydrocarbon	Acetylene	Butadiene	Butene-1
Hydrocarbon order	0.0(110°)	—	—
Hydrogen order	1.0(110°)	1.0(13.5°)	0.58(-18.5°)
E, kcal. mole <sup>-1</sup>	10.6	12.5	4.5
Hydrogen order	—	—	0.56(-18.5°)
E, kcal. mole <sup>-1</sup>	—	—	8.6

the osmium salt and to evaporate off the water in the usual manner even though some decomposition does occur, which results in the loss of a small amount of the metal.

The activation of the catalysts is described in the following section.

### Experimental Results

Two types of system were used: one static, the other dynamic. In the static system, the catalyst rested on the bottom of a cylindrical reaction vessel, which was sealed into a conventional high vacuum system. The reactants were admitted separately and the reaction progress followed manometrically. In the flow system, the catalyst was placed in the form of a thin bed, in a U-shaped reaction

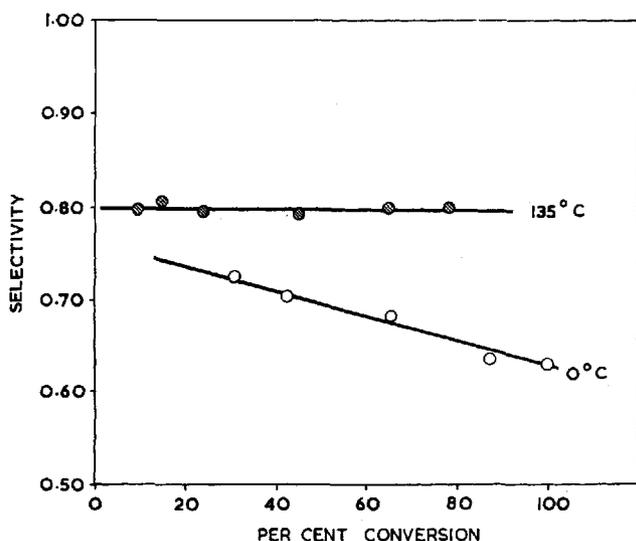


Fig. 1 Variation of selectivity with conversion for acetylene at 135° (hatched circles) and butadiene at 0° (open circles): ruthenium catalyst. Initial hydrocarbon pressure, 50 mm; initial hydrogen pressure, 100 mm

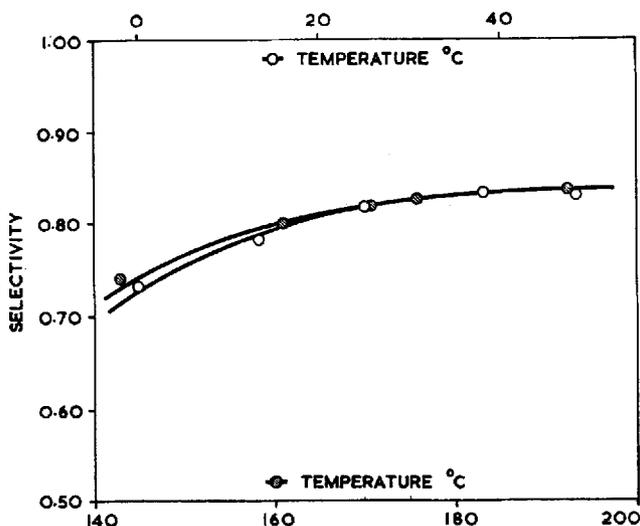


Fig. 2 Variation of selectivity with temperature for acetylene (hatched circles: initial  $H_2/C_2H_2=2$ ) and butadiene (open circles: initial  $H_2/C_4H_6=3$ ): ruthenium catalyst

vessel and hydrogen was allowed to flow through it continually. Shots of hydrocarbon, of known pressure, were admitted into the hydrogen stream and after each had passed through the catalyst bed the products were condensed in a liquid air trap. On warming the trap, the products were passed directly through a gas-liquid chromatography column. A 40 per cent *W/W* acetonyl-acetone on fire-brick (30–60 B.S.S. mesh) column was used at room temperature for the analysis of  $C_4$  hydrocarbons and a silica-gel (40–60 B.S.S. mesh) column, heated to 80°C, for  $C_2$  hydrocarbons.

### Ruthenium Catalysts

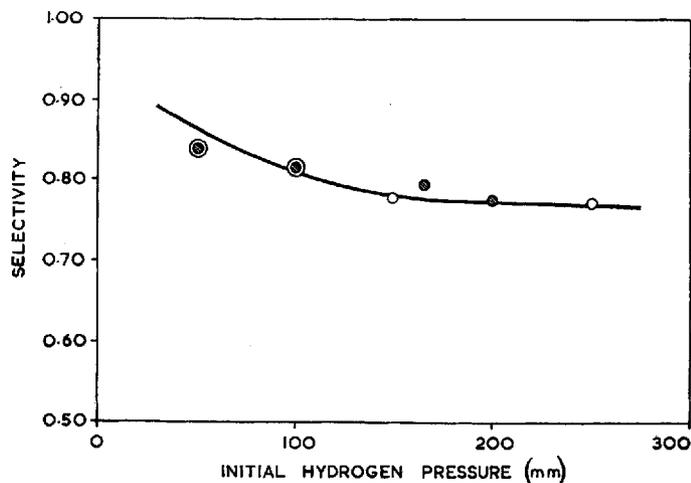
In the flow system the catalysts were activated by reduction of the supported salt at 200°C, the reduction being continued until the effluent gas contained no hydrogen chloride. In the static system, the catalysts were either obtained from samples previously reduced in the flow system, or were reduced *in situ* at 200° for about five hours. The latter tended to show a somewhat greater activity than the former.

The hydrogenation of acetylene, butadiene and the isomerisation and hydrogenation of butene-1 were studied, and the kinetics of these reactions are shown in Table I.

Initial reactions with acetylene were carried

out using 0.3 g of catalyst, but this was active only in the temperature range 170° to 200°C and was subsequently replaced by a 1.0 g sample which was active at 90°C. Addition of the hydrocarbon to the reaction vessel before the hydrogen led to continuous deactivation of the catalyst and most of this work was carried out using the reverse order of addition of the reactants. This procedure led to constant activity and to slightly faster rates. The selectivity, defined as the ratio of olefin produced to total olefin and paraffin, was found to vary slightly from one sample of catalyst to another and also with use of the catalyst, but in all cases was found to be  $0.80 \pm 0.05$  at 150°C. The variations of selectivity with conversion, temperature and initial hydrogen pressure are shown in Figs. 1, 2 and 3 respectively; selectivity was found to be independent of initial acetylene pressure and of the order of addition of reactants. The pressure-fall against time curves showed a continuous decrease in rate and were found to be approximately second order in hydrogen. In reactions with an excess of hydrogen, the rate increased after a certain pressure fall, the increase being due to the hydrogenation of ethylene which is faster than the hydrogenation of acetylene. The point at which this acceleration occurs was found to be independent of temperature and initial hydrogen

Fig. 3 Variation of selectivity with initial hydrogen pressure, for acetylene (hatched circles: 110°) and butadiene (open circles: 13.5°); ruthenium catalyst. Initial hydrocarbon pressure, 50 mm throughout



pressure, and in every case was equal to  $1.40 \pm 0.05$  times the initial acetylene pressure. Analysis of the products at 100 and 200 per cent conversion revealed the presence of about 5 per cent of  $C_3$  and  $C_4$  hydrocarbons, formed by the polymerisation of the acetylene.

For the hydrogenation of butadiene, 0.2 g of catalyst were found to be active at 0°C: butadiene was admitted before the hydrogen. The selectivity for mono-olefin formation was determined and its dependence on conversion, temperature and initial hydrogen pressure is

shown in Figs. 1, 2 and 3 respectively. The pressure-fall against time curves were linear until about 85 per cent conversion, when a slight acceleration was observed. It was observed that up to 100 per cent conversion the distribution of the isomeric butenes remained constant and thence adjusted itself until about 140 to 160 per cent conversion, depending upon the temperature, it reached the equilibrium value obtained from thermal data. The initial distribution appears to be independent of hydrogen pressure but varies

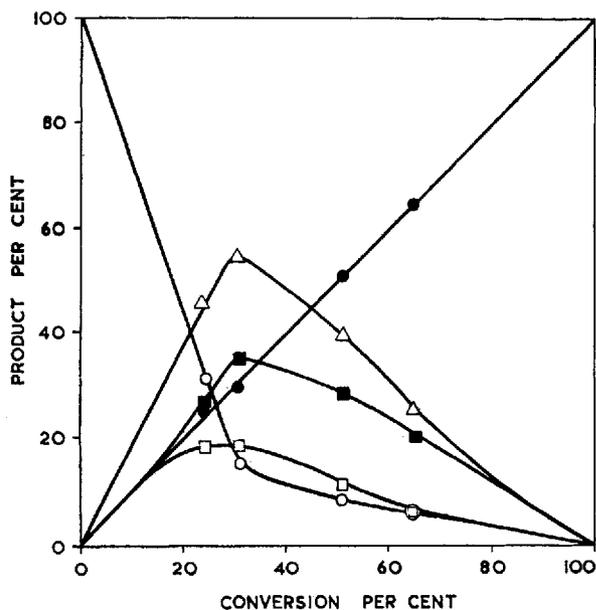


Fig. 4 The hydrogenation of butene-1 over ruthenium at 25°C: variation of hydrocarbon composition with conversion (initial  $H_2/C_4H_8=1$ ). Filled circles, n-butane; open circles, butene-1; filled squares, trans-butene-2; open squares, cis-butene-2; triangles, total butene-2

**Table II**  
**Kinetics of Hydrogenation Reactions over Osmium**

Hydrocarbon	Acetylene	Butadiene	Butene-1
Hydrocarbon order	0.0(165°)	—	—
Hydrogen order	1.0(165°)	1.0(70°)	0.70(25°)
E, kcal. mole <sup>-1</sup>	8.0	10.2	8.6
Hydrogen order	—	—	0.68(25°)
E, kcal. mole <sup>-1</sup>	—	—	9.4

slightly with temperature; at 0°C the distribution of butene-1 : trans-butene-2 : cis-butene-2 is 69 : 20 : 11 per cent, while at 50°C it is 60 : 24 : 16 per cent.

Fig. 4 shows the variation in the composition of the products of the hydrogenation of butene-1 with conversion, using 0.3 g of catalyst at 25°C; it can be seen that isomerisation occurs quite rapidly. From the rate of reaction and the analysis of products it has been possible to calculate the individual velocity constants for hydrogenation and isomerisation. In this way an activation energy and an order of reaction have been calculated for the double bond migration (see Table I).

Both acetylene and butadiene were also hydrogenated in the flow system. The activity

of the catalyst varied from reaction to reaction and it was found impossible to establish any dependence of rate on any of the variables in the system. With both acetylene and butadiene the selectivity was found to be much lower than in the static system. Thus for acetylene a maxi-

mum selectivity of about 0.5 was obtained and with butadiene it varied within the wide limits of 0.35 to 0.75 depending primarily upon the age of the catalyst. By carrying out reactions in the static system using very large excesses of hydrogen and adding the hydrogen first, it has been shown that neither of these factors is responsible for the low selectivities found in the flow system. The most plausible explanation appears to be that, while the catalyst at the bottom of the bed may behave normally with respect to selectivity, by the time the reaction products have passed completely through the bed some of the olefin has been further hydrogenated. With one sample of catalyst, a selectivity of about 1.0 was obtained for butadiene, but

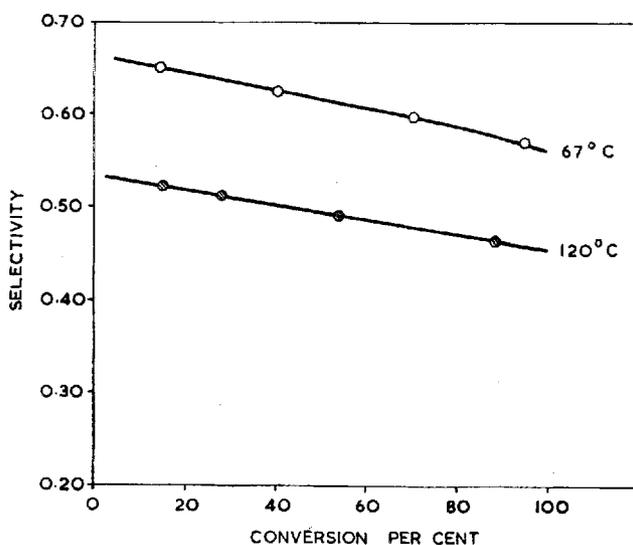
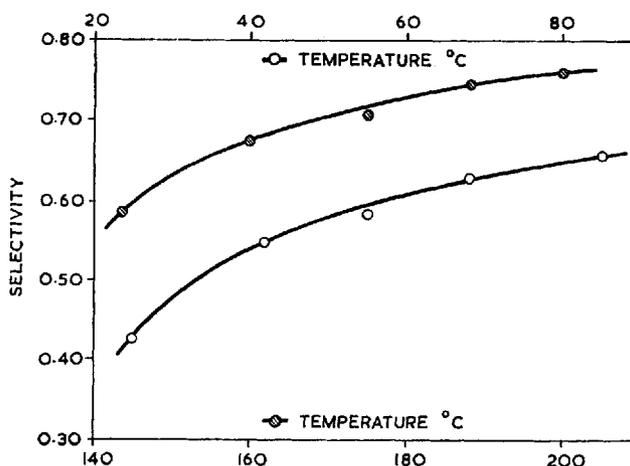


Fig. 5 Variation of selectivity with conversion for acetylene at 120° (hatched circles) and butadiene at 67° (open circles); osmium catalyst, (initial  $H_2$ /hydrocarbon = 5)

Fig. 6 Variation of selectivity with temperature for acetylene (hatched circles: initial  $H_2/C_2H_2=5$ ) and butadiene (open circles: initial  $H_2/C_4H_6=5$ ): osmium catalyst



this is abnormal and is presumably due to selective poisoning of the catalyst, the exact nature of which has not yet been established.

### Results for Osmium Catalysts

The catalysts were activated in an analogous manner to that described for ruthenium and the same reactions were studied. Table II summarises the results obtained.

For the hydrogenation of acetylene it was necessary to use 2.0 g of catalyst, and this was active at 120°C using a fivefold excess of hydrogen. Analysis of the reaction products after 200 per cent conversion revealed that  $C_3$  and  $C_4$  hydrocarbons were present, although they were undetectable at 100 per cent conversion. The polymers constituted about 10

per cent of the total analysed product. The pressure-fall against time curves showed a continuous decrease in rate although the precise shape of the curves during the initial stages of reaction was dependent upon the order of addition of reactants. The dependence of selectivity on conversion, temperature and initial hydrogen pressure is shown in Figs. 5, 6 and 7 respectively. Using a fivefold excess of hydrogen, an acceleration in rate was observed after a pressure fall of 1.75 times the initial acetylene pressure. The dependence of the acceleration point on temperature and initial hydrogen pressure has not been established.

For butadiene 0.3 g of catalyst was found to be active at 25°C using a fivefold excess of

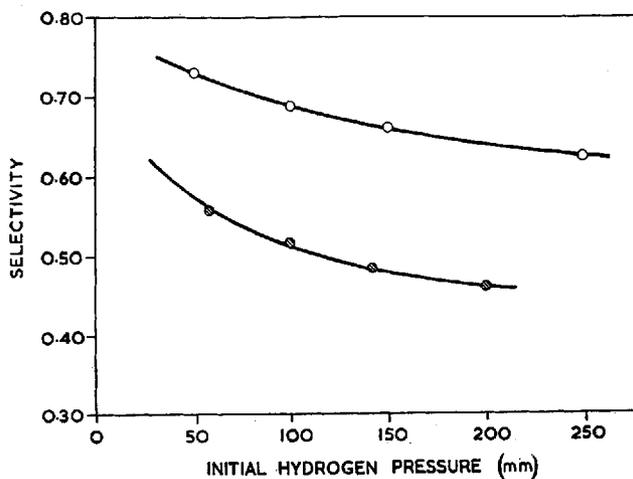


Fig. 7 Variation of selectivity with initial hydrogen pressure, for acetylene (hatched circles: 117°) and butadiene (open circles: 67°). Initial acetylene pressure 30 mm; initial butadiene pressure, 50 mm

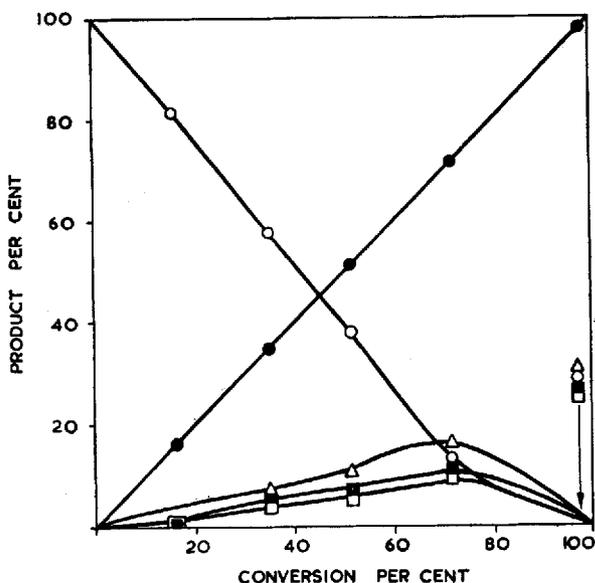


Fig. 8 Hydrogenation of butene-1 over osmium at 25°C: variation of hydrocarbon composition with conversion (initial  $H_2/C_4H_8=5$ ). Filled circles, n-butane; open circles, butene-1; filled squares, trans-butene-2; open squares, cis-butene-2; triangles, total butene-2

hydrogen; the pressure-fall against time plots were linear. The dependence of selectivity on conversion, temperature and initial hydrogen pressure is shown in Figs. 5, 6 and 7 respectively. The distribution of the butenes, which was constant up to 100 per cent conversion, was (at 55°C) 60.0 : 20.5 : 19.5 per cent. The dependence of the distribution on temperature was as with ruthenium.

Fig. 8 shows the distribution of products for the hydrogenation of butene-1; it can be seen that much less isomerisation occurs over osmium than over ruthenium and the maximum isomerisation occurs at a much higher conversion. The activation energy and order have been calculated for the double bond migration and are shown in Table II.

The results obtained for osmium in the flow system showed the same trend as for ruthenium. Both acetylene and butadiene gave a lower selectivity than in the static system and the catalytic activity varied from reaction to reaction.

## Discussion

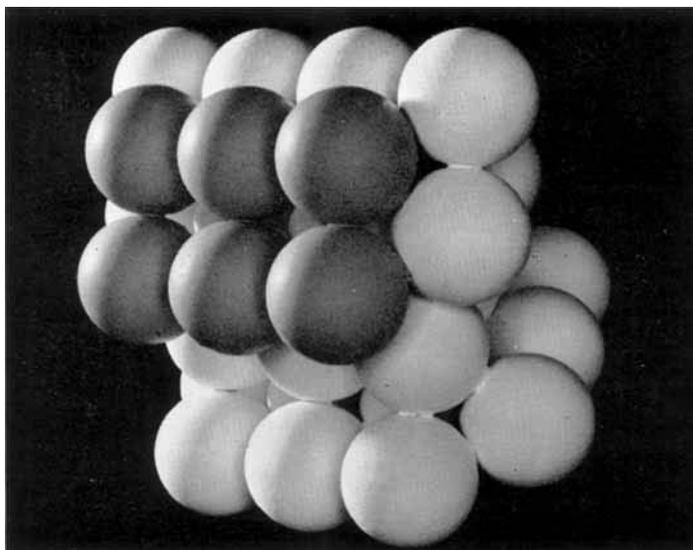
We have established that supported ruthenium and osmium are active catalysts at moderate temperatures for the vapour phase hydrogenation of mono-olefins and a diolefin;

osmium is, however, less active than ruthenium. At high temperatures, both metals are also active for the hydrogenation of acetylene, in disagreement with earlier work (7). The order of reactivity of the hydrocarbons is acetylene < butadiene < butene-1, a sequence which is common to the other platinum metals,

which are only of comparable activity to ruthenium and osmium.

Two points in particular require discussion. The first concerns the role played by the geometric structure of a metal in determining its catalytic behaviour. Now ruthenium and osmium crystallise in the hexagonal close-packed form, while the other platinum metals have the face-centred cubic structure. The previously-found (7) inactivity of ruthenium and osmium in regard to the hydrogenation of acetylene was ascribed to the absence of any spacings in the exposed planes suitable for the adsorption of acetylene. However, even if we assume, as is commonly done, that acetylene prefers to adsorb on the longer interatomic spacings, this need not mean that close-packed hexagonal metals should be inactive, since such spacings are indeed available. Fig. 9 illustrates this: the grey spheres represent atoms forming part of a (30 $\bar{3}$ 4) plane, and this plane contains atoms suitably spaced. Particularly in large crystallites, such planes may not be commonly available, but in view of the relatively small difference in activity between say ruthenium and rhodium for acetylene hydrogenation, it is to say the least questionable whether such geometric considerations play any part at all. A final

Fig. 9 A model of a portion of a close-packed hexagonal crystal. The grey spheres represent part of a  $(30\bar{3}4)$  plane, which contains spaces suitable for adsorbing acetylene



decision cannot yet be reached, but at least the question has been reopened.

The second point requiring discussion concerns the similarities which exist between, on the one hand, ruthenium, rhodium and palladium, and, on the other, osmium, iridium and platinum. The second row metals are characterised by (i) a fairly high selectivity in the hydrogenation of acetylene and butadiene, and (ii) a marked tendency to encourage double-bond migration, whereas the third row metals show (i) lower selectivities than the metal immediately above it, and (ii) little tendency to promote double-bond migration. The interconnection between selectivity and rate of double-bond migration

is readily understood in a very qualitative way, and will be discussed in a subsequent article. The reasons underlying the differences between the second and third row metals are, however, much more difficult to understand, but this problem will be returned to again.

We may summarise the work reported here by saying that the study of the catalytic behaviour of ruthenium and osmium is playing a vital role in increasing our understanding of the behaviour of the other platinum metals.

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