

The Oxidation State of Rhenium and Its Role in Platinum-Rhenium Reforming Catalysts

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The increasing environmental concern about the pollution caused by motor vehicles has focused attention on catalytic reforming as a means of improving the octane number of lead-free petrol. Much research has been carried out in recent years aimed at improving the conventional platinum-alumina reforming catalysts. The most significant advance has turned out to be the discovery of a new family of catalysts in which a second metal, usually rhenium, is added to the platinum (1). A bimetallic platinum-rhenium reforming catalyst was first introduced (2, 3) by Chevron in February 1967, but several such catalysts are now available.

Rhenium activated catalysts have many advantages over conventional catalysts, but in particular they offer greatly improved temperature stability and product distribution selectivity (4, 5) (Figure 1). Some of the applied aspects of platinum-rhenium catalysts have been described previously in this Journal (4), but the purpose of this review is to examine the experimental evidence that is available concerning the oxidation state of rhenium and its role as a promoter in platinum reforming catalysts.

The influence of rhenium in prolonging the lifetime of platinum-rhenium catalysts has variously been ascribed to (i) the formation of an alloy which is less active than pure platinum for dehydrogenation (6-9); (ii) the presence of Re^{4+} which is active for the hydrogenation of carbon deposits (10, 11); or (iii) the stabilisation of platinum crystallites against sintering (12, 14).

Contained within these various proposals are two important questions. First, is the rhenium reduced to the metal? Second, if rhenium metal is produced, does it form an alloy with platinum?

The Interaction between Rhenium and the Support

Unsupported rhenium oxides are easily reduced to the metal by hydrogen at 400 to 500°C. With alumina supported oxides, however, the situation is complicated because of a strong interaction with the support (15). Evidence for such an interaction in $\text{Re}/\text{Al}_2\text{O}_3$ catalysts **which have been calcined** is found in the fact that Re_2O_7 , which is a volatile compound, is not detected in the gas phase even when these catalysts are regenerated in air at 550°C (16-18). On the other hand, Bolivar et al (7) claim that there is a loss of rhenium from catalysts that have not been calcined before reduction. The calcination treatment is obviously important and will be referred to again.

Oxidation State of Rhenium before Hydrogen Treatment

Yao and Shelef (18) have presented evidence from chemisorption experiments which shows that prior to calcination the rhenium on an alumina support is probably present in two forms, a crystalline three-dimensional phase of Re_2O_7 , and a dispersed two-dimensional phase containing Re^{4+} . Calcination would be expected to lead to the evaporation and loss of the crystalline Re_2O_7 . However, if there

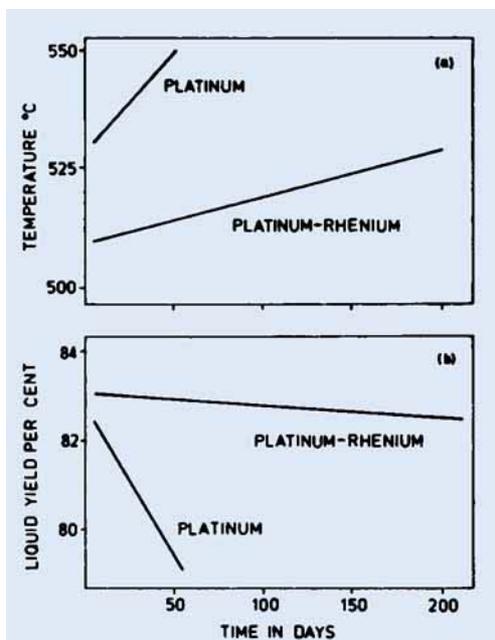


Fig. 1: (a) Temperature required to maintain a given octane quality as a function of operating time (after Reference 4); (b) liquid yield as a function of operating time (after Reference 4)

is available a sufficiently large surface of free alumina, an evaporated crystal of Re_2O_7 could react with this surface to produce more, dispersed, Re^{4+} . This would account for the low loss of Re_2O_7 during oxidative regeneration. It would also mean that in a typical commercial catalyst, having a rhenium content of only about 0.2 per cent, the majority of the rhenium would be present initially in the dispersed form as Re^{4+} . It should be noted, however, that McNicol (19) has found that for a catalyst containing 0.2 per cent rhenium, the oxidation state of rhenium is 7+ after calcination in air at 525°C.

Are Both Forms of Rhenium Reducible?

The crystalline form of Re_2O_7 is easily reduced to the metal at around 300 to 350°C (7, 8, 9, 18). The dispersed Re^{4+} is much more

difficult to reduce but in dry hydrogen reduction proceeds slowly at 500°C, and complete reduction can be obtained (18, 19, 20). On the other hand, in moist hydrogen it appears that reduction of rhenium below the 4+ oxidation state is difficult, if not impossible (10, 21).

Effect of Calcination Treatment on the Minimum Temperature for Reduction

In the Absence of Platinum

The calcination treatment has an important influence on the reducibility of rhenium oxides on alumina. After drying at 110°C (7-9) or after calcining at 330°C (18), rhenium oxide on alumina can be reduced at 320 to 330°C. However, Yao et al (18) found that the maximum rate of reduction occurred at 550°C after a dispersion treatment which involved heating the catalyst for 16 hours in nitrogen at 500°C. Further calcination in air at 500°C for two hours produced two reduction maxima, one at 350°C and the other at 550°C (Figure 2). McNicol (19) observed a single reduction peak at 550°C after calcining his samples in air at 525°C for two hours before reduction. The absence of a low temperature peak is probably because the amount of rhenium present was only 0.2 per cent as compared with 1.2 per cent in the samples used by Yao et al.

The conclusions are that low temperature calcination results in an easily reduced form of rhenium (Re_2O_7 ?) but that calcination above 500°C converts much of the rhenium to a more stable oxide form (Re^{4+} ?), particularly in catalysts containing small amounts of rhenium.

In the Presence of Platinum

Platinum is well known as a catalyst for the reduction by hydrogen of a number of metal oxides. Such a catalytic effect has been observed for platinum-rhenium catalysts dried at 110°C (7). In the presence of platinum the reduction of rhenium commences at much lower temperatures, 160 to

180°C instead of 330°C. On the other hand, after high temperature calcination no catalytic effect due to the platinum is observed (10, 19).

The conclusion to be drawn from this is that platinum can catalyse the reduction of three-dimensional crystalline supported rhenium oxide, but has little effect on the reduction of dispersed rhenium oxide. Consequently, in an industrial catalyst with a metal content of about 0.2 per cent the interaction between platinum and rhenium during reduction is likely to be minimal.

Do Rhenium and Platinum Form an Alloy?

Under the most favourable conditions—low calcination temperature, high rhenium loading—it has been clearly established (8, 9) that there is an interaction between rhenium and platinum leading ultimately to alloy formation. For calcined catalysts there are some discrepancies in reported work. Sovostin et al (13) and Bursian (12) claim that rhenium increases the dispersion of platinum on alumina, which implies some form of interaction, although not necessarily to the extent of alloy formation. However, McNicol (19) reports no interaction between platinum and rhenium during reduction, although subsequent alloy formation between migrating and coalescing particles could still occur, albeit slowly (22).

It appears that platinum and rhenium can form alloys on an alumina surface and do so when there is an interaction during the reduction stage. Whether alloy formation occurs in industrial catalysts is not certain, although some form of direct interaction between platinum and rhenium seems probable.

The Role of Rhenium

Johnson (10, 21) has suggested that Re^{4+} species on the alumina surface can hydrogenate carbon residues and thus increase the lifetime of the platinum catalyst. However, since the addition of rhenium increases not only the lifetime but also the selectivity and

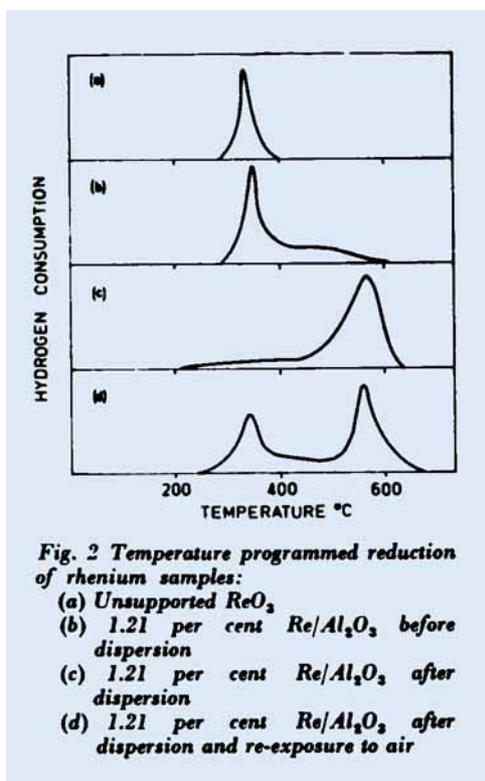


Fig. 2 Temperature programmed reduction of rhenium samples:

- (a) Unsupported ReO_3
- (b) 1.21 per cent $\text{Re}/\text{Al}_2\text{O}_3$, before dispersion
- (c) 1.21 per cent $\text{Re}/\text{Al}_2\text{O}_3$, after dispersion
- (d) 1.21 per cent $\text{Re}/\text{Al}_2\text{O}_3$, after dispersion and re-exposure to air

activity of the catalyst it is difficult to see how this could occur if the only function of rhenium was to hydrogenate carbon residues.

A number of other workers have argued that it is the formation of a platinum-rhenium alloy that is responsible. Assuming that alloy formation occurs, the influence of rhenium could arise either because of a change in the electronic charge at the platinum atoms, or because the rhenium atoms dilute the platinum atoms on the surface.

The direction of electron transfer between rhenium and platinum is difficult to predict and both $\text{Pt}\delta^-$ (8) and $\text{Pt}\delta^+$ (23, 24) have been suggested. Electron withdrawal from platinum seems more likely since the magnetic susceptibility of platinum is increased by alloying with rhenium. $\text{Pt}\delta^+$ would have a high activity for reforming reactions since these tend to proceed through carbonium ion intermediates which are formed with electron donation to the metal atom.

A dilution effect will arise because rhenium atoms in the surface of an alloy particle will reduce the number of platinum atom clusters. At least two and probably three or more contiguous platinum atoms are required for coke formation, whereas reforming may occur on isolated platinum atoms (23). Therefore, the effect of adding rhenium would be to decrease the rate of coking without affecting the reforming reaction. It is probable that rhenium exerts both an electronic and a structural influence on platinum. The electronic effect will result in an increase in the intrinsic activity of the platinum, and may also affect the selectivity. The geometric effect will result in an increase in the lifetime of the catalyst, and may again affect the selectivity.

Conclusions

Recent research on platinum-rhenium reforming catalysts illustrates how pure research aimed at giving a better understanding of an industrial system can completely circumscribe the problem and yet not provide

a clear answer. The basic question is whether or not platinum and rhenium form an alloy under the conditions likely to be encountered in an industrial reactor. The answer obtained is that under **dry laboratory conditions** an alloy may be formed. However, bearing in mind the ubiquity of water and its influence on solid state reactions, one should perhaps be cautious in assuming that the results of carefully controlled laboratory experiments will be applicable in an industrial context.

Perhaps the clearest indication that there is at least some form of interaction between platinum and rhenium under industrial conditions comes from the fact that platinum-rhenium catalysts are more **active** in reforming reactions than pure platinum catalysts.

In conclusion, the balance of the available evidence supports the existence of a direct interaction between platinum and rhenium. Whether this interaction results in alloy formation, or involves, for example, the formation of a more highly dispersed form of platinum, is still not certain.

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