

“Carbons and Carbon Supported Catalysts in Hydroprocessing”

BY EDWARD FURIMSKY (IMAF Group, Ottawa, Ontario, Canada), Royal Society of Chemistry, Cambridge, U.K., 2008, 176 pages, ISBN 978-0-85404-143-5, £95.00

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Elemental carbon is known in a variety of forms that range from diamond gemstones through C_{60} fullerene and graphite to carbon nanotubes, but to those working with catalysts the most familiar are probably high surface area forms known as ‘activated charcoals’. The very high surface areas of porous charcoals made from wood and peat, as well as those derived from more exotic materials such as coconut husks, are well suited as catalyst supports and each have specific desirable properties. They are used widely to prepare platinum group metal (pgm) catalysts (1) that typically contain only a few per cent of pgm yet have very high activities at low temperatures. This is because, not only do pgms have high intrinsic catalytic activity, but they can also be very finely dispersed over activated charcoals, as extremely small crystallites that provide high surface areas of the active metal. These catalysts, and especially those containing palladium, have been used extensively for many years in organic preparative chemistry (2), and today they have important roles in hydrogenation and hydrogenolysis reactions. They even find application in some carbon–carbon bond forming processes (3) and potentially also in direct carbonylation reactions (4). In spite of their importance in pgm-based catalysts, carbon supports are less well known in base metal catalysts. One reason for this is that, over time, there can be a tendency for metals like cobalt, iron or nickel to form carbides, especially at higher temperatures, and this leads to a loss of catalytic activity.

The present small book, as its title suggests, is about the catalytic activity of carbons (and especially activated charcoals) and metal compounds supported on carbons, with a focus on catalytic hydroprocessing reactions of crude oils. These

reactions include hydrogenation, hydrocracking, hydrodesulfurisation, hydrodenitrogenation, and hydrodemetallation processes. Huge quantities of hydroprocessing catalysts are employed in refineries, and the most common ones are sulfided cobalt/molybdenum and nickel/molybdenum formulations, and to a much lesser extent their tungsten analogues, supported on aluminas with various promoters. Reflecting the importance of very low sulfur hydrocarbon fuels, there is a vast literature on hydroprocessing catalysts, and especially on the nature of the active sulfide phases present in the operating catalysts (5, 6).

Carbon-Supported Hydroprocessing Catalysts

After a short general introductory chapter outlining the basic structures of graphite, carbon black, diamond, activated carbons, C_{60} fullerene and carbon nanotubes, there is another short chapter entitled ‘Industrial Carbons’ that provides details of the physical properties of each of the carbon forms. The next chapter briefly discusses the structure and composition of traditional hydroprocessing catalysts and the cobalt/molybdenum phases involved in hydrodesulfurisation, and contrasts this with what is known about their carbon-supported counterparts. Here, the metal–carbon interactions are likely to be weakened by the presence of metal–sulfur bonds, and while this might be thought to inhibit deactivation *via* carbide formation, it could well open up other deactivation paths such as loss of surface area. The influence of physical properties like support pore size is also discussed.

The fourth chapter is concerned with the ability of carbons to absorb, activate and transfer

active hydrogen *via* C–H bonds at high temperatures. At the lower temperatures normally used for carbon-supported pgm catalysts, these reactions must be much less important than the activation of hydrogen by the supported pgms. Indeed in the presence of platinum, palladium or rhodium, dissociative hydrogen chemisorption takes place on the metal, followed by spillover onto the carbon surface to form weakly bonded mobile H atoms. Most of the cited examples are systems based on cobalt/molybdenum formulations, although other interesting catalysts are referred to.

The following chapter, entitled ‘Catalytic Activity of Carbons’, begins with a comparison of coking tendencies of cobalt/molybdenum species supported on alumina and supported on activated charcoal. In use, activated charcoal-based catalysts have a very much smaller rate of coke formation from anthracene than do alumina-based catalysts, and this difference is attributed to the relative acidity of the supports – the alumina being acidic while the carbon is said to be neutral. However, it is clear that such benefits in reactions with real feeds are not always apparent, and this may at least in part be because the acid/base behaviour of activated charcoals can vary enormously depending on their origin and the treatments they have undergone.

The sixth chapter, ‘Carbon Supported Catalysts’, is concerned with the preparation of carbon supported hydroprocessing catalysts, and it covers most of the conventional preparative methods. Techniques used to characterise these carbon-supported catalysts are also discussed, and they include a range of spectroscopic and adsorption/desorption methods as well as catalytic activity measurements. The results presented highlight that this is a complicated area of catalysis, with multiple parameters influencing the catalyst’s activity in practice. The next chapter, ‘Kinetics and Mechanism of Hydroprocessing Reactions’, deals with hydrogenation of aromatics, hydrodesulfurisation, hydrodenitrogenation, hydrodeoxygenation and hydrodemetallation reactions, and reinforces the conclusion that this is a complex area of catalysis. Several tables of rate constants with various feeds over conventional and carbon-supported catalysts are provided; however, there is little

discussion about the intimate mechanisms of these reactions. The eighth chapter, ‘Catalyst Deactivation’, reminds the reader that coking reactions are an important deactivation process for conventional hydroprocessing catalysts, and that their carbon-supported counterparts can be less prone to this deactivation mode.

The penultimate chapter on ‘Patent Literature’ is surprisingly brief, being only one and a half pages long and with fewer than ten patents cited – this, it is said, reflects the rather limited patent literature on carbon-supported hydroprocessing catalysts. However, there are in fact many more related published patents than those listed, and it is not clear what criteria were applied to produce this short list. The final two-page chapter provides some ‘Conclusions’, including the proposal that the activity of carbon-supported catalysts is based on their ability to adsorb and activate hydrogen. In this regard, carbon blacks are said to be more able to activate hydrogen than activated charcoals, which in turn are more active than graphite. And, of course, this is much enhanced by the presence of metal species, especially palladium and platinum.

Commercial Applications

This book contains some thought provoking information, and it will certainly be of interest to those involved with carbon-based catalysts. In some instances, there appear to be benefits from using carbon-supported hydroprocessing catalysts, although the fundamental reasons for this are not always delineated, nor are guide rules provided. Commercially activated charcoals often have various promoters incorporated on their surfaces, and may have undergone an oxidative pre-treatment that gives a high dispersion of the active species when it is applied. In the context of this book it is unclear what effects these treatments have on, for example, carbon-supported sulfided cobalt/molybdenum hydroprocessing catalysts.

It is, however, clear that carbon supports have attracted much more attention in areas other than hydroprocessing reactions, and with the exception of promoted carbon-supported ruthenium catalyst for ammonia synthesis (7), the most successful

carbon-supported catalysts are used at low temperatures. The hydroprocessing catalysts discussed in this book, on the other hand, operate at relatively high temperatures. Under these hydrogenating conditions, a major practical problem could be gasification of the support itself to give methane or other hydrocarbon species, and this should not be overlooked when considering carbon-supported catalysts for hydrogenation applications involving high hydrogen partial pressures and high temperatures. It is claimed in this book that carbon gasification is slow under typical hydrodesulfurisation conditions, although over several months' operation some irreversible structural changes may take place. However, little information about this is available. Potential practical complications such as this are not explored in any detail, although before these carbon-supported hydroprocessing catalysts are considered for industrial applications it is paramount that they be better understood, though perhaps not to the level of detail that pgms on carbons are understood from their widespread use and characterisation over many years.

References

- 1 A. J. Bird, 'Activated Carbon Supports', in "Catalyst Supports and Supported Catalysts: Theoretical and Applied Concepts", ed. A. B. Stiles, Butterworth-Heinemann, Stoneham, Massachusetts, U.S.A., 1987, pp. 107–137
- 2 See for example: J. C. Chaston and E. J. Sercombe, *Platinum Metals Rev.*, 1961, 5, (4), 122
- 3 See for example: L. S. Liebeskind and E. Peña-Cabrera, *Org. Synth., Collect. Vol.*, 2004, 10, 9
- 4 H. M. Colquhoun, D. J. Thompson and M. V. Twigg, "Carbonylation: Direct Synthesis of Carbonyl Compounds", Plenum Publishing Corp, New York, U.S.A., 1991
- 5 H. Topsøe, B. S. Clausen and F. E. Massoth, "Hydrotreating Catalysis", eds. J. R. Anderson and M. Boudart, *Catalysis Science and Technology*, Volume 11, Springer Verlag, Berlin, Germany, 1996
- 6 J. Scherzer and A. J. Gruia, "Hydrocracking Science and Technology", Marcel Dekker, New York, U.S.A., 1996
- 7 S. R. Tennison, 'Alternative Noniron Catalysts', in "Catalytic Ammonia Synthesis: Fundamentals and Practice", ed. J. R. Jennings, *Fundamental and Applied Catalysis Series*, Plenum Press, New York, U.S.A., 1991, pp. 303–364

The Reviewer



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