Bimetallic effects in the liquid-phase hydrogenation of 2-butanone

J.P. Breen [a,*], R. Burch [a], K. Griffin [b], C. Hardacre [a], M. Hayes [b], X. Huang [a], S.D. O'Brien [a]

[a] *CenTACat, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, N. Ireland, UK*
[b] *Johnson Matthey plc, Orchard Road, Royston, Hertfordshire, SG8 5HE, UK*

Abstract

A series of bimetallic Ru-containing monometallic and bimetallic catalysts were prepared and tested for their activity for the hydrogenation of 2-butanone to 2-butanol at 30 °C and 3 bar H_2. RuPt bimetallic catalysts were the most active for the reaction, with a ratio of 5 wt% Ru:1 wt% Pt on activated carbon (AC) found to be optimum. The activity of this bimetallic catalyst was more than double that of the sum of the activities of the monometallic Ru and Pt catalysts, providing evidence of a "bimetallic" effect. Structural analysis of the bimetallic catalysts revealed that they consisted of clusters of particles of the order of 1–2 nm. Extended X-ray absorption fine structure analysis showed that there were two types of particle on the surface of the bimetallic RuPt catalyst, specifically monometallic Ru and bimetallic RuPt particles. For the bimetallic particles, it was possible to fit the data with a model in which a Ru core of 1.1 nm is enclosed by two Pt-rich layers, the outer layer containing only 13 at% Ru. Pretreatment of the monometallic and bimetallic catalysts in hydrogen had a significant effect on the activity. Both the bimetallic and monometallic Ru-based catalysts showed a trend of decreasing activity with increasing temperature of prereduction in hydrogen. This loss of activity was almost fully reversible by exposure of the catalysts to air after reduction. The changing activity with exposure to different gas phase environments could not be attributed to changes in particle size or surface composition. It is proposed that the introduction of hydrogen results in a gradual smoothing of the surface and loss of defect sites; this process being reversible on introduction of air. These defect sites are particularly important for the dissociative adsorption of hydrogen, potentially the rate-determining step in this reaction.
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1. Introduction

Bimetallic catalysts are at present the subject of considerable interest in heterogeneous catalysis, due to the fact that their catalytic properties can be superior to those of monometallic catalysts for many reactions [1]. The discovery of bimetallic catalysts has, in fact, been one of the major technical developments in heterogeneous catalysis [2] and it is now widely acknowledged that the addition of the second metal provides a method of controlling the activity, selectivity, and stability of the catalysts in certain reactions [3]. Various bimetallic combinations have been used successfully for different reactions. Pt–Re catalysts are used commercially as reforming catalysts. Binary Pt alloys, such as Pt–Ru or Pt–Sn, have been suggested as catalysts

for the fabrication of fuel cell anodes with increased CO tolerance [4,5]. Bimetallic catalysts have been studied for various hydrogenation reactions [6–12]. Thomas and co-workers have done much research on the preparation and characterisation of ruthenium [13] and ruthenium-containing bimetallic catalysts [14–18]. They have pioneered a method of anchoring well-defined bimetallic ensembles within mesoporous silica pores to produce catalysts that are active and selective for various hydrogenation reactions. The activity was found to be dependent on the nature of the second metal added to ruthenium, the ratio of ruthenium to the second metal, and the cluster size. They found that Ru/Pt bimetallic catalysts were particularly active for the hydrogenation of cyclohexene [19].

It is not clear exactly what role the metal promoter plays in enhancing catalytic activity; it may have a direct role as an active centre for the reaction or may simply modify the active component. It is also not clear if the two metals form alloys,

if surface segregation of one element occurs, or if the two elements are randomly distributed on the surface of the catalyst [20]. Several authors have suggested a synergistic effect whereby catalytic performance is enhanced by the synergy between the component elements at the nanoscale [21–23]. The role of the second metal is sometimes simply to overcome a limiting side reaction or to promote a certain part of the reaction. In some cases the promoter metal shows no activity for the chosen reaction by itself but greatly enhances the activity when added to the existing catalyst. Iwasawa and co-workers used Sn-modified Rh catalysts for NO dissociation and NO–H_2 reaction [24]. They acknowledged that Sn metal has no significant catalytic activity by itself, because it does not interact with H_2, hydrocarbons, CO, or NO, but found that Sn can be used as a promoter for SiO_2-supported transition metal catalysts to enhance catalytic performance. Another possibility is that the addition of a second metal changes the morphology of the active metal. When one metal is deposited on another, one observes a number of different phenomena. The deposited metal may form islands on the substrate or may alloy into the first or deeper layers [25]. Although it was presumed that alloy formation was the essence of the promotional effect in bimetallic catalysts, more recent studies have shown that in some cases alloy formation is not desired. Waszczuk et al. [26] have found that a decorated Pt/Ru catalyst is twice as active for methanol electro-oxidation (in terms of current density and turnover frequency) as the commercial alloy catalyst, both of which have nominally identical Pt:Ru ratios. They concluded that ruthenium atoms present at the edge of Pt nano-sized islands display significantly enhanced activity for the CO poison removal compared with the active sites on a Pt/Ru alloy.

Consequently, it is important to characterise the size, structure, and distribution of the metal particles of these bimetallic catalysts in an attempt to understand the correlation between microstructure and catalytic properties. Characterisation of catalysts by the traditional bulk techniques can be very difficult because of the microscopic nature of the particles. This is especially true for bimetallic systems, which can be complicated by the presence of several metal phases [27]. For example, Rolison et al. [28] performed bulk and surface analyses of several commercial and industrial Pt–Ru/C electrocatalysts and highlighted the need to use a combination of techniques to characterise the catalysts; in particular, they found that X-ray diffraction (XRD) analysis on its own could give misleading results.

In this paper, Pt–Ru bimetallic catalysts are characterised by various techniques, including transmission electron microscopy (TEM), extended X-ray absorption fine structure (EXAFS) analysis, XRD, and X-ray photoelectron spectroscopy (XPS). The results of the characterisation are correlated with the activity of the catalysts for the hydrogenation of 2-butanone after a series of pretreatment procedures. Hydrogenation of 2-butanone was chosen as a test reaction primarily because the reaction is 100% selective to 2-butanol under mild conditions of temperature and pressure and thus allows comparison of activities of catalysts without complications due to selectivity.

2. Experimental

2.1. Catalyst preparation

The catalyst preparation method used depended primarily on whether the metals were impregnated onto the high-surface area graphite (HSAG) or activated carbon (AC) support. For the monometallic 5 wt% ruthenium/activated carbon catalyst, the wood-based activated carbon was slurried in deionised water, and an aqueous solution of Na_2RuO_4 was added. The slurry was allowed to cool and settle before being filtered and dried. A similar procedure was used to prepare the monometallic 1 wt% Pt/AC catalyst, using a Pt nitrate precursor. For the bimetallic AC-supported catalysts, the 5 wt% Ru/AC was used as the starting material. Aqueous solutions of the metallic nitrate precursor salts were allowed to contact the 5 wt% Ru/AC catalyst for 1 h before being dried in an oven overnight. The monometallic graphite-supported catalysts were prepared by making up the required solutions from chloride precursors. These salt solutions were added to the (HSAG) slurry, and reduced with formaldehyde or sodium hypophosphite. The catalysts were allowed to settle, then washed, filtered, and dried. A similar procedure was used to prepare the bimetallic HSAG-supported catalysts, except in this case a mixed solution of metal salts was made up and then added to the graphite slurry. Table 1 summarises details of the preparation procedures for all of the catalysts. It is important to note that in what follows, the term "fresh catalyst" refers to the catalyst state after drying the catalyst.

2.2. Catalytic tests

The hydrogenation reactions were performed in a 300 cm^3 Parr stainless steel autoclave with a maximum pressure of

Table 1
Summary of catalyst preparation variables

Metal loading	Metal precursor salts	Support	Reducing agent	Notation
5% Ru	Na_2RuO_4	Activated carbon	None	5Ru/AC
5% Ru 1% Rh	Na_2RuO_4 a nitrate of Rh	Activated carbon	None	5Ru1Rh/AC
5% Ru 1% Pd	Na_2RuO_4 a nitrate of Pd	Activated carbon	None	5Ru1Pd/AC
5% Ru 1% Pt	Na_2RuO_4 a nitrate of Pt	Activated carbon	None	5Ru1Pt/AC
5% Ru 2% Pt	Na_2RuO_4 a nitrate of Pt	Activated carbon	None	5Ru2Pt/AC
5% Ru 0.1% Pt	Na_2RuO_4 a nitrate of Pt	Activated carbon	None	5Ru0.1Pt/AC
5% Ru 0.5% Pt	Na_2RuO_4 a nitrate of Pt	Activated carbon	None	5Ru0.5Pt/AC
1% Pt	A nitrate of Pt	Activated carbon	None	1Pt/AC
5% Pt	Chloride	Graphite	Formaldehyde	5Pt/HSAG
4% Ru 1% Pt	Chlorides	Graphite	Sodium hypophosphite	4Ru1Pt/HSAG
1% Ru 4% Pt	Chlorides	Graphite	Sodium hypophosphite	1Ru4Pt/HSAG
5% Ru	Chloride	Graphite	Sodium hypophosphite	5Ru/HSAG