Available online at www.sciencedirect.com
SCIENCE DIRECT®

PERGAMON

Polyhedron 22 (2003) 3–7

POLYHEDRON

www.elsevier.com/locate/poly

Gas sensor activity of ArgoGel resin-supported pentaruthenium clusters

Catherine M.G. Judkins [a], Kevin A. Knights [b], Brian F.G. Johnson [a,*], Yolanda R. de Miguel [b,*]

[a] *Chemistry Department, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*
[b] *Chemistry Department, King's College London, Strand, London WC2R 2LS, UK*

Received 26 April 2002; accepted 27 June 2002

Abstract

A new sensor has been prepared by coordination of the pentaruthenium cluster, $[Ru_5C(CO)_{15}]$, to phosphine ligands supported on ArgoGel resin. These cluster-containing beads exhibit a characteristic colour change and FTIR shift when treated with the gases H_2S, SO_2 or CO, demonstrating an important potential use for such supported metal species in gas sensing devices.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Clusters; Ruthenium; Sensors; ArgoGel resins; Supported transition metals; Gas sensing

1. Introduction

Polymer resin beads are of considerable industrial interest, having found a wide range of uses in combinatorial chemistry and in the development of new heterogeneous catalysts [1,2]. An extensive range of such resins is commercially available, each resin displaying characteristics that may be matched to a specific process or application. However, research into such resins has been largely targeted at the afore-mentioned areas and it is therefore of interest to seek other important fields in which these materials may be employed. In continuation of our previous work [3], we have chosen to explore further possible applications of transition metal clusters supported on amphiphilic polystyrene/divinyl benzene resins, which have polyethylene glycol (PEG) chains grafted to them (eg. ArgoGel). These were chosen because they displayed good flexibility and accessibility to the active sites during our earlier catalytic studies.

Ruthenium cluster species are known to react with a variety of donors and, in the case of the pentaruthenium cluster, $[Ru_5C(CO)_{15}]$, such reactions occur readily and bring about a change in the geometrical structure of the cluster unit. This change is well documented [4] and can be monitored by routine spectroscopic methods, thus providing a route to possible chemical sensors. Recent work by Dyson and coworkers [5] has shown a possible application for the above pentaruthenium cluster in the removal of sulfur compounds from fuels under ambient, homogeneous conditions but, as yet, no investigations under heterogeneous conditions have been carried out.

In this communication, we wish to report: (i) a synthetic route to a phosphine-functionalised ArgoGel amine resin and its subsequent treatment with $[Ru_5C(CO)_{15}]$; (ii) the full characterisation of the cluster containing species; and (iii) our initial investigations into its capacity as a sensor for the gases H_2S, CO and SO_2.

2. Results and discussion

Conversion of the terminal amine sites of the ArgoGel resin to diphosphine groups was achieved by an adaptation of a literature procedure [6]. Paraformaldehyde and diphenylphosphine were mixed in methanol

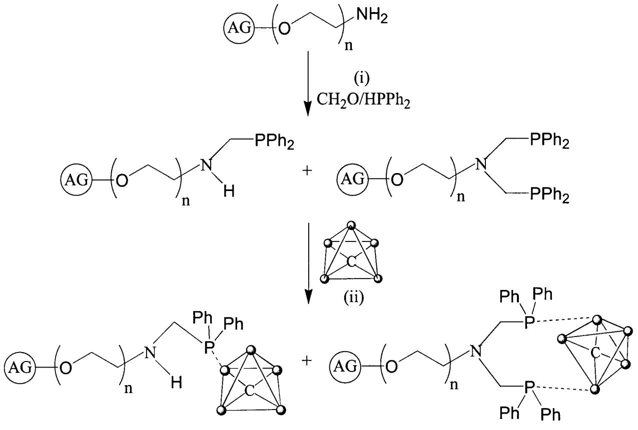
---

* Corresponding authors. Tel.: +44-1223-336-337; fax: +44-1223-336-017 (B.F.G.J.); Tel.: +44-20-7848-1180; fax: +44-20-7848-2810 (Y.R.M.)

E-mail addresses: bfgj1@cam.ac.uk (B.F.G. Johnson), yolanda.demiguel@kcl.ac.uk (Y.R. de Miguel).

0277-5387/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0277-5387(02)01325-6

and the intermediate formed was added via cannula to the ArgoGel amine (1 g, 0.37 mmol g^{-1} N) in toluene.[1] The mixture was stirred under an inert atmosphere for 3 h at 65 °C, followed by a further 15 h at room temperature. Removal of the solvent and washing with methanol, ethanol and finally pentane yielded the desired product with supported phosphine ligands, as characterised by gel phase ^{31}P, ^{13}C and HR-MAS ^{1}H NMR spectroscopy (using dry $CDCl_3$ as the solvent). The ^{31}P NMR spectrum[2] showed peaks at δ -26.3 and -27.1 ppm (ratio 1.2:1), corresponding to the supported phosphine ligand. The appearance of two signals in this region is believed to be due to a mixture of both bidentate and monodentate phosphine ligands, as indicated in Scheme 1. The ^{1}H NMR spectrum showed peaks in the region δ 7.48–7.82 ppm, confirming the presence of the phosphine phenyl groups and at δ 3.53 ppm (d, $J = 11.5$ Hz), assigned to the NCH_2PPh_2 protons. Elemental analysis showed the amount of nitrogen on the bead to be 0.53% (0.38 mmol g^{-1}) and the amount of phosphorus to be 0.99% (0.32 mmol g^{-1}), thus indicating that not all NH sites available on the bead had undergone reaction (42% yield). This N:P ratio of 1.2:1 from the microanalysis was in good agreement with the ratio of the two supported phosphine ligand peaks in the ^{31}P NMR spectrum. Hence, the peak at δ -26.3 ppm could be tentatively assigned to the monodentate species and the peak at δ -27.1 ppm could be assigned to the bidentate product. These results were similar to those obtained in previous work using the hexaruthenium cluster, $[Ru_6C(CO)_{17}]$ [3].



Scheme 1. Formation of ArgoGel-supported phosphine ligands and possible coordination modes of the $[Ru_5C(CO)_{15}]$ cluster. AG = ArgoGel resin, ◒ = Ruthenium, CO ligands omitted for clarity. *Reagents and conditions*: (i) CH_3OH, PhMe, 65 °C (3 h), r.t. (15 h), Ar; (ii) CH_2Cl_2, r.t., 5 days, Ar.

The phosphine-derivatised ArgoGel beads were then reacted with excess $[Ru_5C(CO)_{15}]$[3] in dichloromethane, resulting in an immediate colour change in the beads from cream to dark red (Fig. 1). The reaction was continued for 5 days to allow all available phosphine sites to react with the cluster. After washing several times with dichloromethane and pentane the beads were dried under vacuum and characterised by FTIR and gel phase NMR spectroscopy, as well as microanalysis. The single bead FTIR spectrum confirmed the presence of the carbonyl ligands on the cluster moiety, showing peaks at 2052, 2010, 1998, 1983, and 1973 cm^{-1}. The ^{13}C NMR spectrum also confirmed the presence of carbonyl groups, with peaks at δ 199.2 and 195.7 ppm. The absence of peaks at δ -26.3 and -27.3 ppm in the ^{31}P NMR spectrum indicated that all free phosphine sites had coordinated to the metal cluster, and this coordination resulted in the appearance of new peaks at δ 34.1, 36.3 (d) and 40.2 ppm (ratio 1.2:0.3:1). The appearance of several peaks is once again consistent with the different coordination modes of both the monodentate and bidentate phosphine ligands to the cluster. Two examples of these modes are given in Scheme 1. Bidentate coordination to a single ruthenium atom is found in the reaction between $[Ru_5C(CO)_{15}]$ with the ligand $PPh_2(CH_2)_3PPh_2$, but bidentate bridging across the base of the square pyramid is often the more thermodynamically favoured mode [7]. A related model species, $[\{(CH_2)_4N(CH_2PPh_2)_2[Ru_5C(CO)_{12}]\}_2]$, prepared recently [8] showed the two phosphine atoms and the nitrogen atom coordinating to three basal ruthenium atoms. Since the nitrogen atoms are also accessible in the ArgoGel phosphine product, this could be a further possible mode of coordination for the clusters. In view of the earlier spectroscopic data for this material prior to treatment with the cluster, we may assume that the peak at δ 34.1 ppm corresponds to the monodenate ligand coordinated to the cluster, and that at δ 40.2 ppm to the bidentate ligand coordinated to the cluster in the possible modes discussed above. Since X-ray analysis is not viable for polymer resin species, the exact nature of the cluster coordination modes could not be determined and must remain uncertain. This is, however, immaterial to the main thrust of the work viz. the interaction with substrates such as H_2S or CO. It is the metal cluster framework, not the phosphine ligand that undergoes polyhedral rearrangement; hence the

---

[1] All reactions were carried out under an inert atmosphere using dried, distilled solvents. Paraformaldehyde (44.5 mg, 1.5 mmol) and diphenylphosphine (0.38 ml, 2.2 mmol) were first reacted in MeOH (10 ml) and the reaction mixture was transferred to the ArgoGel resin suspended in toluene (40 ml). After the reaction was complete, the beads were thoroughly washed and dried in vacuo prior to characterisation.

[2] Due to the highly air sensitive nature of this intermediate, peaks corresponding to phosphorus oxide were also apparent between δ 28 and 31 ppm, despite reactions and sample handling being carried out in an inert atmosphere.

[3] 1.5 equiv. of the cluster were used.

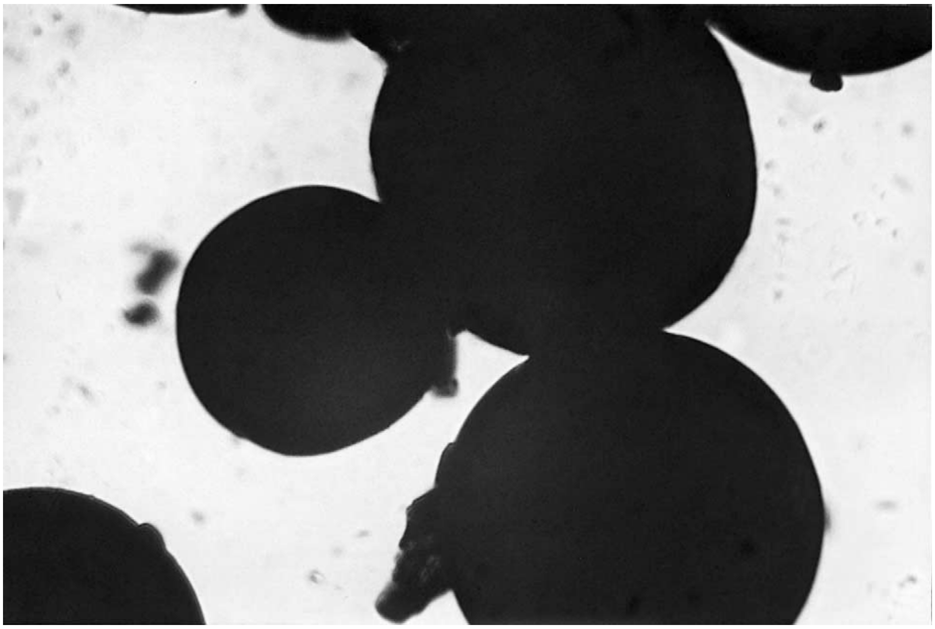


Fig. 1. ArgoGel-Ru_5 beads before treatment with gas.

nature of the binding to the resin is not believed to influence sensor activity. The phenyl proton peaks in the ^{1}H HR-MAS NMR shifted to δ 7.55–7.92 ppm upon coordination to the cluster and ICP-AES analysis revealed the mass percent of ruthenium on the beads to be 10.58 (0.21 mmol g^{-1}). Microscopy showed that the spherical nature of the resin remained intact (Fig. 1).

Previous work using [$Ru_5C(CO)_{15}$] in *solution* has shown that it readily reacts with dihydrogen sulphide, resulting in a rearrangement of the square based pyramid structure of the metal framework [5]. Our initial efforts were therefore targeted at the same reaction, using our *supported* pentaruthenium moiety to see if any changes in geometry or colour could be detected. In addition, we also extended our studies to include the gases carbon monoxide and sulfur dioxide, both of which are known to produce adducts with ruthenium clusters [9,10]. In a typical reaction, the ArgoGel–pentaruthenium complex (20 mg) was added to dried dichloromethane (20 ml) and the appropriate gas was bubbled into the solution for 2 h. The reactions were monitored by single bead FTIR spectroscopy and any colour change was noted.

In the reaction with H_2S, the beads turned from dark red to a dark, green/black colour, as shown in Fig. 2. The single bead FTIR spectrum (taken at 2 h) showed a broad peak in the carbonyl region, consisting of several peaks: 2043, 2034, 2021, 2010, 1998, 1986, 1974 and 1965 cm^{-1}. The peaks at 2010, 1998, and 1974 cm^{-1} may be assigned to the unreacted, supported Ru_5 moiety, implying that only the most accessible cluster sites had reacted with the H_2S gas and that those sites deeper in the bead structure had not yet reacted. It is significant that on further agitation of the H_2S-saturated dichloromethane suspension, all remaining Ru_5 sites underwent reaction. Thus, the FTIR spectrum taken after 2 days showed a much sharper series of carbonyl peaks at 2036, 1982 and 1965 cm^{-1} and no peaks corresponding to the unreacted Ru_5 species, thus confirming that the reaction had reached completion. Importantly, it is clear that given the colour change and the IR shift (see above), the complete reaction of all sites is not a prerequisite for H_2S detection.

Upon stirring the dichloromethane suspension of Ru_5-functionalised beads with CO a different colour change occurred, with the beads turning from dark red to pink/red as shown in Fig. 3. The FTIR spectrum (taken at 2 h) showed several peaks in the carbonyl region at 2052, 2043, 2033, 2020, 1998, 1986 and 1974 cm^{-1}. Again, it would appear that only the most accessible Ru_5 sites had reacted with the CO, resulting in the appearance of two new peaks in this region. The saturated CO suspension of beads was stirred for a further 2 days in order to allow the Ru_5 sites deeper in the bead matrix to react. The FTIR spectrum then showed a set of peaks at 2051, 2033, 2018, 1990 and 1982 cm^{-1}, indicating that the reaction had achieved completion. Again, as discussed above, it is clear that only partial reaction (of the most accessible sites) is required for the dramatic colour change to be observed.

In a similar reaction with SO_2, the dark red beads showed a considerable lightening in colour, becoming orange/red as seen in Fig. 4. As with the previous reactions, the FTIR spectrum (taken at 2 h) of the SO_2 treated beads showed that a reaction had taken place but was not complete. The broad series of carbonyl stretching frequencies appeared at 2063, 2042, 2021,

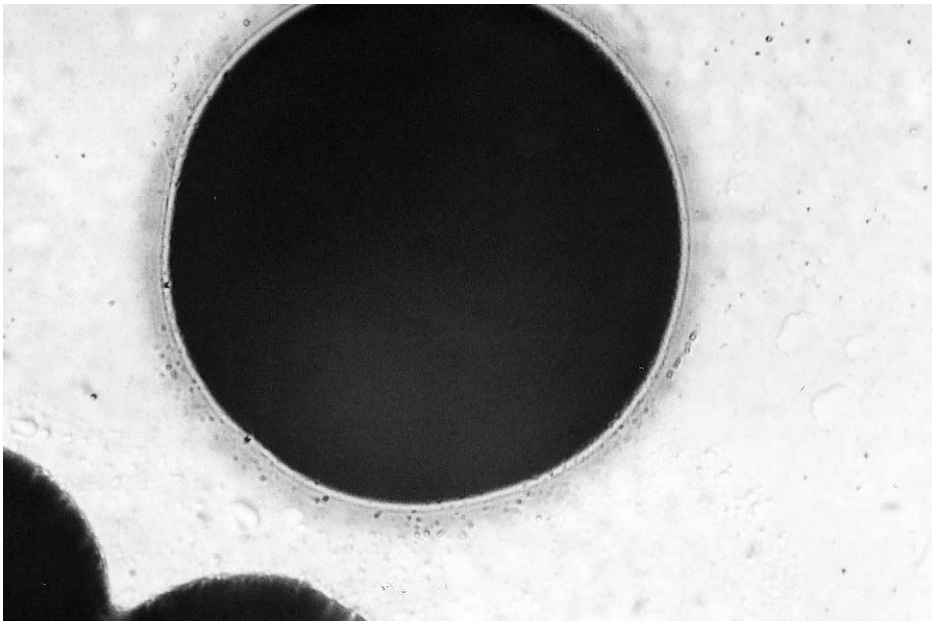


Fig. 2. ArgoGel-Ru_5 beads after reaction with H_2S.

2009, 1999, 1986 and 1974 cm^{-1}. However, after further agitation of the beads in the SO_2-saturated dichloromethane solution, the FTIR spectrum showed a sharp set of carbonyl peaks at 2073, 2059, 2037, 2019 and 2005 cm^{-1}.

These observations reveal the potential of the cluster-containing beads to function as a sensor for the gases H_2S, SO_2 and CO. It is most likely that all reactions involve the polyhedral rearrangement of the $[Ru_5C(CO)_{15}]$ species from its original square pyramid to a bridged-butterfly metal core. Further steps are in progress to enhance the efficiency of these reactions, since not all available sites reacted immediately. Nevertheless, the characteristic colour changes exhibited by these materials demonstrates their potential as chemical sensor devices, and also the possibility of dehydrosulfurisation under ambient, *heterogeneous–homogeneous* conditions.

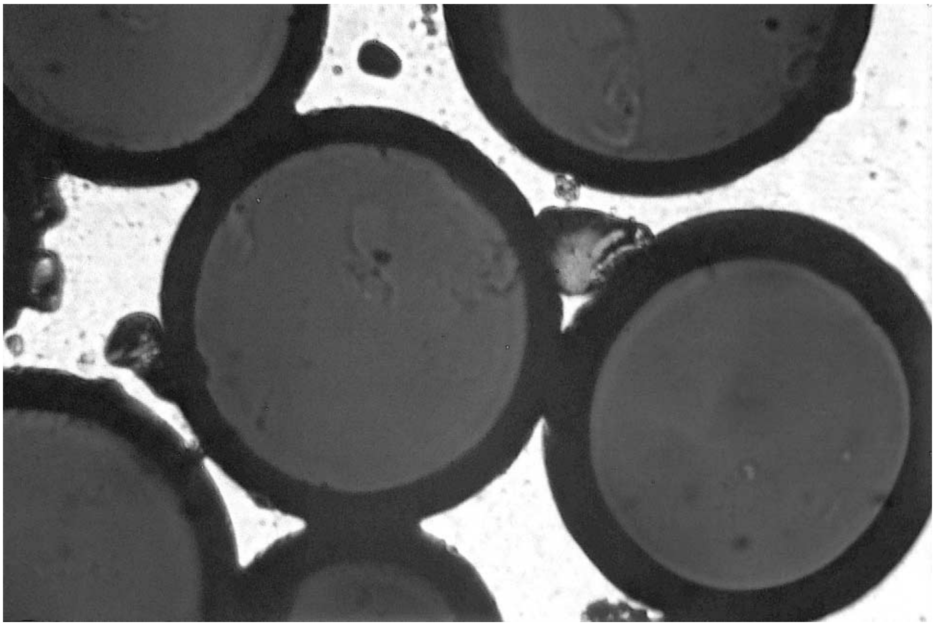


Fig. 3. ArgoGel-Ru_5 beads after reaction with CO.

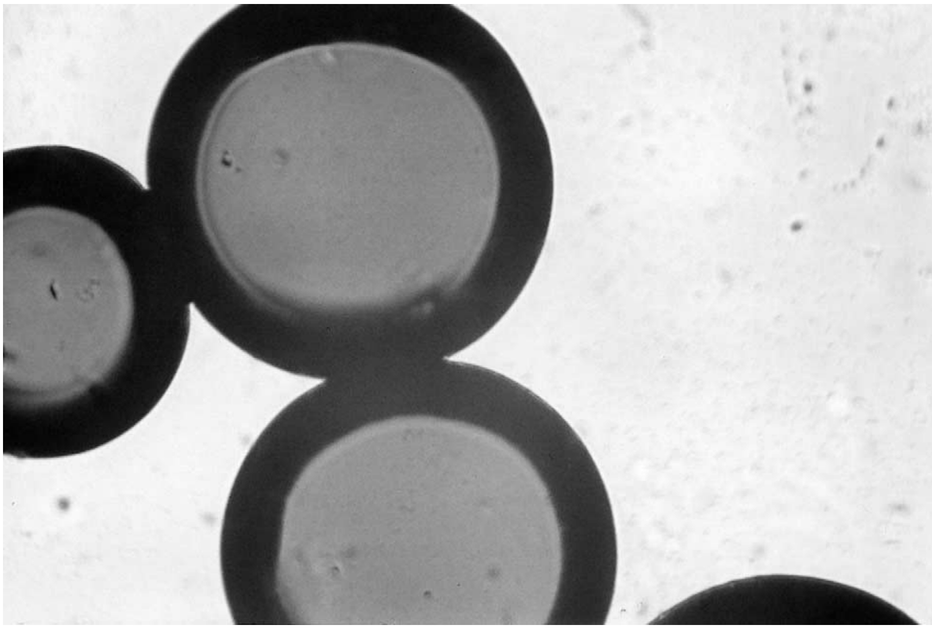


Fig. 4. ArgoGel-Ru_5 beads after reaction with SO_2.

Acknowledgements

We would like to thank Dr Andrew Bond for his assistance with obtaining the photographs and Dara Henry for running the single bead FTIR spectra. We are also grateful to the EPSRC and ICI (C.M.G.J.) and King's College London (K.A.K.) for financial assistance, as well as the Royal Society for a Dorothy Hodgkin Fellowship (Y.D.M.).

References

[1] S.V. Ley, I.R. Baxendale, R.N. Bream, P.S. Jackson, A.G. Leach, D.A. Longbottom, M. Nesi, J.S. Scott, R.I. Storer, S.J. Taylor, J. Chem. Soc., Perkin Trans. I 23 (2000) 3815.

[2] Y.R. deMiguel, E. Brule, R.G. Margue, J. Chem. Soc., Perkin Trans. I 23 (2001) 3085.

[3] C.M.G. Judkins, K.A. Knights, B.F.G. Johnson, Y.R. deMiguel, R. Raja, J.M. Thomas, Chem. Commun. (2001) 2624.

[4] For example: B.F.G. Johnson, J. Lewis, J.N. Nicholls, J. Puga, K.H. Whitmire, J. Chem. Soc., Dalton Trans. (1983) 787.

[5] A.J. Bailey, S. Basra, P.J. Dyson, Green Chem. 1 (1999) 1, 31.

[6] M.T. Reetz, G. Lohmer, R. Scwickardi, Angew. Chem., Int. Ed. Engl. 36 (1997) 1526.

[7] J. Evans, B.P. Gracey, L.R. Gray, M. Webster, J. Organomet. Chem. 240 (1982) C61.

[8] N. Feeder, J. Geng, P.G. Goh, B.F.G. Johnson, C.M. Martin, D.S. Shephard, W. Zhou, Angew. Chem., Int. Ed. Engl. 39 (2000) 1661.

[9] T. Chihara, H. Kubota, M. Fukumoto, H. Ogawa, Y. Yamamoto, Y. Wakatsuki, Inorg. Chem. 36 (1997) 5488.

[10] B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J.N. Nicholls, J. Puga, P.R. Raithby, M.J. Rosales, M. Schröder, M.D. Vargas, J. Chem. Soc., Dalton Trans. (1983) 2447.