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In the Lab

Ductile Metal Oxides Impregnated on Magnetite: New Catalysts in Organic Synthesis

Johnson Matthey Technology Review features new laboratory research

Diego J. Ramón is a Professor in the Department of Organic Chemistry at the University of Alicante, Spain. His research focuses on the development of catalysts based on transition metal oxides impregnated on the surface of magnetite and their application to different reactions of general interest in Organic Chemistry. He has published over 100 papers.

About the Research

The particle size of active material in heterogeneous catalysts has a great impact on selectivity, efficiency and specificity. In fact, nano-catalysts have properties different from the macroscopic systems due not only to different specific area but also to the presence of electric charges over them, and above all to the presence of extremely distorted bonds.

Metallic oxides, including magnesia, alumina, silica, zirconium oxide and cerium oxide, are supports commonly used in the preparation of nano-metal catalysts. Although magnetite (Fe $_3$ O $_4$), like any other metal oxide, could be used as a suitable support, as has been demonstrated in other areas including medicine, biology and materials science, its use in organic chemistry has been minimal, due to the axiomatic idea that magnetite is unstable. As a support, magnetite has a unique advantage due to the superparamagnetic behaviour of its nanoparticles that allows its recovery and confinement by using a simple magnet or electromagnetic field. This property should make magnetite an ideal support material.

About the Researcher



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Ramón's group has designed a simple, robust and inexpensive methodology for the impregnation of different transition metal oxides on the surface of magnetite. The impregnation protocol allows all active nano-metallic species to be on the surface of the catalyst, and therefore increases their activity. The group has prepared catalysts derived from cobalt, copper,

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ruthenium, palladium, osmium, iridium and platinum (Figure 1). These versatile catalysts have been used to carry out several transformations of general interest in organic chemistry (Figure 2), among others Suzuki-Miyaura cross-coupling, the multicomponent reductive amination of aldehydes, hydrosilylation of alkynes, borylation of olefins, benzofurans and indole synthesis, and the alkylation of amines through a borrowing hydrogen strategy. Moreover it has been possible to achieve the first practical cross-alkylation of primary alcohols using iridium impregnated on magnetite.

When an external magnetic field is applied, the superparamagnetic particles of the magnetite acquire magnetisation, but it is lost when the magnetic field is retired. So, magnetite nanoparticles can be isolated easily from the reaction media using an external magnet (Figure 3) after the reaction. In many cases, the catalyst could be recovered by the simple use of a magnet and recycled in successive cycles with the same initial activity. Figure 4 shows the yields obtained with the different catalysts in ten successive reaction cycles.

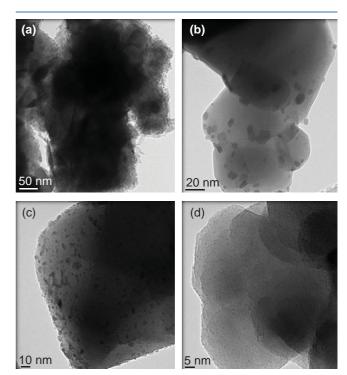


Fig. 1. Transmission electron microscopy (TEM) images of magnetite-derived catalysts: (a) copper; (b) ruthenium; (c) palladium; and (d) iridium

Fig. 2. Application of magnetite and transition metal oxides impregnated on magnetite to different organic synthesis reactions

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Fig. 3. Easy recovery of the catalyst after reaction by using a magnet

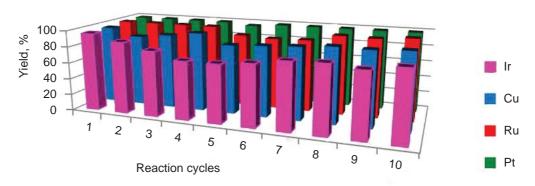


Fig. 4. Obtained yields in selected reactions after recycling different catalysts

Selected Publications

- J. M. Pérez and D. J. Ramón, *Adv. Synth. Catal.*, 2014, **356**, (14–15), 3039
- J. M. Pérez, R. Cano and D. J. Ramón, RSC Adv., 2014, 4, (46), 23943
- R. Cano, J. M. Pérez and D. J. Ramón, *Appl. Catal. A: Gen.*, 2014, **470**, 177
- R. Cano, M. Yus and D. J. Ramón, *Tetrahedron*, 2013, **69**, (34), 7056
- J. M. Pérez, R. Cano, M. Yus and D. J. Ramón, *Synthesis*, 2013, **45**, (10), 1373
- J. M. Pérez, R. Cano, M. Yus and D. J. Ramón, *Eur. J. Org. Chem.*, 2012, (24), 4548
- R. Cano, M. Yus and D. J. Ramón, *Chem. Commun.*, 2012, **48**, (61), 7628
- R. Cano, M. Yus and D. J. Ramón, *ACS Catal.*, 2012, **2**, (6), 1070
- R. Cano, M. Yus and D. J. Ramón, *Tetrahedron*, 2012, **68**, (5), 1393
- R. Cano, M. Yus and D. J. Ramón, *Tetrahedron*, 2011, **67**, (42), 8079
- R. Cano, D. J. Ramón and M. Yus, *Synlett*, 2011, (14), 2017

- R. Cano, D. J. Ramón and M. Yus, *J. Org. Chem.*, 2011, **76**, (14), 5547
- R. Cano, D. J. Ramón and M. Yus, *Tetrahedron*, 2011, **67**, (30), 5432
- R. Cano, D. J. Ramón and M. Yus, *J. Org. Chem.*, 2010, **75**, (10), 3458
- M. J. Aliaga, D. J. Ramón and M. Yus, *Org. Biomol. Chem.*, 2010, **8**, (1), 43
- R. Martínez, D. J. Ramón and M. Yus, *Adv. Synth. Catal.*, 2008, **350**, (9), 1235

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