Advanced one-step methods for the preparation of tailored heterogeneous catalysts – the case of oxide-based olefin metathesis catalysts

Damien P. Debecker

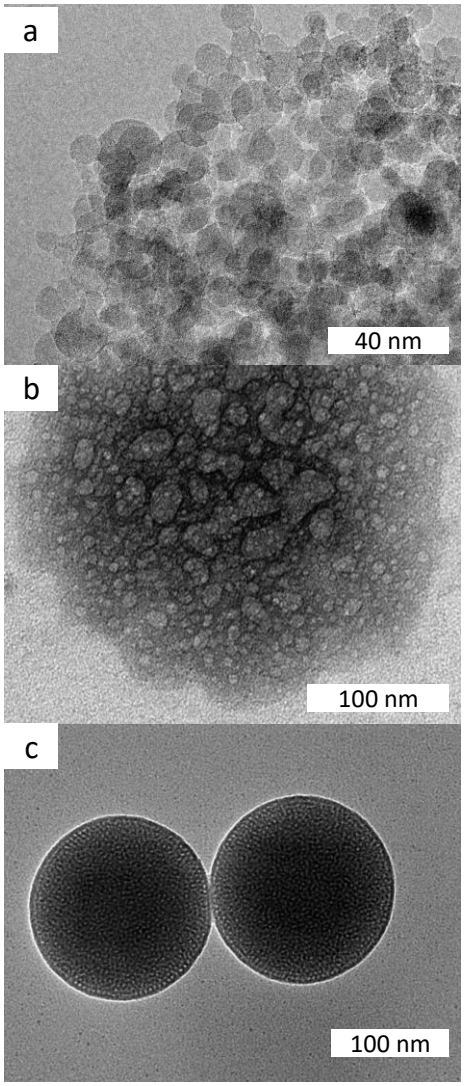
Institute of Condensed Matter and Nanoscience - MOlecules, Solids and reactiviTy (IMCN / MOST). Université catholique de Louvain. Croix du Sud 2 box L7.05.17, 1348 Louvain-La-Neuve, Belgium (email: damien.debecker@uclouvain.be)

Olefin metathesis is a crucial reaction catalyzed by metal carbenes. To obtain a highly active heterogeneous metathesis catalyst, one can (i) design highly active organometallic complexes and graft them onto an appropriate carrier or (ii) use the most classical preparation routes to supported oxide catalyst (impregnation/calcination) in which a small proportion of the metal oxide will turn into active carbenes when contacted with the olefin[1]. In the petrochemical industry, the second strategy – which yields cheap and robust catalysts – is preferred even though the activity is modest. In this communication we show that there is a way through. After studying the factors that dictate the genesis of active metathesis sites in supported MoO_3-catalysts (thus identifying the limitations of these formulations)[2], we explore three innovative routes to prepare more active catalysts.

Firstly (a) flame spray pyrolysis[3] yields non porous silica-alumina particles at the surface of which Mo oxide species condenses in the flame.[4] At very low MoO_3 loading (1 wt.%), the method produces highly dispersed MoO_x species which exhibit very high TOF. At higher loading the specific activity drops because inactive oligomers and crystals build up.

Secondly (b) non-hydrolytic sol-gel[5] yields mesoporous Si-Al-Mo mixed oxides in one step and in the absence of a template.[6] We show that Mo species migrate toward the surface during calcination and are stabilized as highly dispersed and thus highly active species even at high MoO_3 loading. Record specific activity were obtained.[7]

Thirdly (c) an original sol-gel route processed in an aerosol in the presence of a template[8] yields ordered mesoporous Si-Al-Mo mixed oxides which possess unprecedented properties and high metathesis activity.[9]



[1] K. Amakawa, S. Wrabetz, J. Kröhnert, G. Tzolova-Müller, R. Schlögl, A. Trunschke, *J. Am. Chem. Soc.* **2012**, *134*, 11462-11473. [2] D. P. Debecker, M. Stoyanova, U. Rodemerck, A. Leonard, B.-L. Su, E. M. Gaigneaux, *Catal. Today* **2011**, *169*, 60-68.[3] B. Schimmoeller, S. E. Pratsinis, A. Baiker, *ChemCatChem* **2011**, *3*, 1234-1256. [4] D. P. Debecker, B. Schimmoeller, M. Stoyanova, C. Poleunis, P. Bertrand, U. Rodemerck, E. M. Gaigneaux, *J. Catal.* **2011**, *277*, 154-163. [5] D. P. Debecker, P. H. Mutin, *Chem. Soc. Rev.* **2012**, *41*, 3624-3650. [6] D. P. Debecker, K. Bouchmella, C. Poleunis, P. Eloy, P. Bertrand, E. M. Gaigneaux, P. H. Mutin, *Chem. Mater.* **2009**, *21*, 2817-2824. [7] D. P. Debecker, K. Bouchmella, M. Stoyanova, U. Rodemerck, E. M. Gaigneaux, P. Hubert Mutin, *Catal. Sci. Technol.* **2012**, *2*, 1157-1164. [8] C. Boissiere, D. Grosso, A. Chaumonnot, L. Nicole, C. Sanchez, *Adv. Mater.* **2011**, *23*, 599-623. [9] D. P. Debecker, M. Stoyanova, F. Colbeau-Justin, U. Rodemerck, C. Boissière, E. M. Gaigneaux, C. Sanchez, *Angew. Chem. Int. Ed.* **2012**, *51*, 2129-2131.