Gas Phase Glycerol Valorisation over Ceria Nanocrystals with Well-defined Morphologies

L. Smith, N. F. Dummer, M. Douthwaite, D. Willock, S. H. Taylor, G. J. Hutchings
Cardiff Catalysis Institute, Cardiff University, Cardiff, USA

Abstract

The rapid expansion of the biodiesel market has resulted in a glycerol surplus, since the process involves the transesterification of triglycerides with methanol to produce fatty acid methyl esters and glycerol, with glycerol comprising 10 w/w % of the total product yield. Recent work by the Hutching's group [Nature Chemistry **7**, 1028–1032 (2015)] showed that glycerol (both pure and crude grade) could be converted to a crude aqueous methanol mixture by its reaction with water over a basic oxide catalyst. This process is operated at atmospheric pressure without the requirement of an external reductant, and can provide a renewable route for transforming an undesirable by-product of biodiesel production into a reagent used in biodiesel production. Whilst CeO_2 was shown to be an effective catalyst for this transformation, little effort was made to optimize the catalyst, so this work focuses on the effect of ceria morphology and the exposed surface planes of ceria, on the reactivity of glycerol, and consequent methanol production. Ceria nanocrystals with well-defined morphologies were prepared; HRTEM was used to identify the morphologies and exposed crystal planes, which were found to be (100) for the cubes, (110) and (100) for the rods, and (111) and (100) for the polyhedra. These materials were tested as catalysts for the conversion of glycerol to methanol at a space velocity of 3600 h^{-1} between 320 – 400 °C. Product distribution relates strongly to glycerol conversion, thus it was difficult to draw meaningful conclusions from these reactions, as significantly lower conversion was observed over the cubes. Very similar product distributions were achieved over the rods and polyhedra, although the methanol space time yield was superior over the polyhedra (201 g h^{-1} kg^{-1} at 400 °C) vs. the rods (164 g h^{-1} kg^{-1} at 400 °C) due to the improved carbon balance. To achieve similar levels of glycerol conversion the space velocities were increased to 9000 h^{-1} over the rods and polyhedra. Glycerol conversion of 15 % was achieved over all three morphologies, allowing direct comparison of product distributions; similar product selectvities were observed over the rods and polyhedra, with the major product identified as hydroxyacetone, the main intermediate observed on the route to methanol, initiated by the loss of glycerol's secondary hydroxyl group. In contrast, the major product identified over the cubes was acrolein, a double dehydration product of glycerol, initiated by the loss of the terminal hydroxyl group. Additionally, 1,2-propanediol was observed over the rods and polyhedra, with 1,3-propanediol observed over the cubes, representing the reduction products of hydroxyacetone and 3-hydroxypropanal respectively, adding further evidence for the different reaction pathways observed. In-situ studies and complementary modelling are currently being performed to investigate the adsorption of glycerol on the different surfaces to further understand the high acrolein and low methanol selectivities observed over ceria nanocubes.