

Bimetallic CoRe in APD silica aerogels for ammonia decomposition.

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Production, storage and transportation of hydrogen is one of the great challenges in the 21st century, and represent a solution to provide new clean energy to end our dependence upon fossil fuels. Production of hydrogen from liquid ammonia is widely studied due to its high hydrogen content and relative ease of storage. Low temperature ammonia decomposition is favoured by metal supported on more or less porous carriers such as ruthenium supported on carbon nano tubes (Ru/CNT) with different promoters, showing promising efficacy for low temperature (below 470 K) in situ hydrogen production.¹ For this purpose, bimetallic phases of cobalt and rhenium supported on silica aerogel have been synthesised through co-precipitation and then dried with the ambient pressure drying method (APD).

Silica aerogels are ultra-porous materials consisting mainly of air, exhibiting interesting surface characteristics such as hydrophobicity.^{2, 3} The structure consists of interconnected silica particles that form mesopores and micropores. Other properties include high surface area, low thermal conductivity and hydrophobicity. Preparation of an active phase within this 3D carrier has several benefits affecting both reactivity and economy. High dispersions is often obtained on functional inner surfaces and imposed growth limitations can prevent sintering which can greatly affect both reducibility and reversibility of the metal phase.^{4, 5}

The reducibility of cobalt and rhenium was studied using *in situ* XAS of the cobalt K-edge and rhenium L_{III}-edge (BM31, Swiss-Norwegian Beamlines, European Synchrotron Radiation Facility) and the reduction profile analysed using multivariate curve resolution analysis (MCR). The reduction of both metals occurs simultaneously and over a lower temperature range (300-350°C) than their monometallic analogues, suggesting a synergistic effect occurs promoted by the 3D support. While rhenium is completely reduced by 75% hydrogen, a low multiplicity Co-O shell

is still present at 600°C at the Co K-edge. This might be due to partially oxidised surface species or interaction with the aerogel support.⁶

EXAFS analysis show a high degree of Co-Re mixing in the CoRe@aerogel during both pre-treatment and ammonia decomposition with the major phase being Co-Re clusters less than 1 nm. We believe the activity is governed by the presence of the bimetallic Co-Re pair. Interestingly an increase in the multiplicity of a Co-O/N shell is observed during ammonia decomposition indicative of surface adsorbed nitrogen or increased interaction with the support.

References:

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