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SELECTIVE CATALYSTS FOR GLYCEROL DEHYDRATION

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There has been an increased interest over the last decade for replacing fossil based feedstock's with renewable ones. There are several such feedstock's that are currently being investigated such as cellulose, lignin, hemicellulose, triglycerides etc. However, when trying to perform selective reactions an as homogeneous feedstock as possible is preferable. One such feedstock example is glycerol, a side-product from biofuels production, which is a tri-alcohol and thus has much flexibility for reactions, e.g. dehydration, hydrogenation, addition reactions etc. Glycerol in itself is a good starting point for fine chemicals production being non-toxic and available in rather large quantities [1-2]. A key reaction for glycerol valorisation is the dehydration of glycerol to form acrolein, an unsaturated C₃ aldehyde, which may be used for producing acrylic acid, acrylonitrile and other important chemical products. It has recently been shown that pore-condensation of glycerol is an issue under industrial like conditions, leading to liquid-phase reactions and speeding up the catalyst activity and selectivity loss [3]. To address this issue, modified catalyst materials have been prepared where the relevant micro and meso pores have been removed by thermal sintering; calculations have shown that pores below 45 Å may be subject to pore condensation. The catalyst starting material was a 10% WO₃ by weight supported on ZrO₂ in the form of beads 1–2 mm and it was thermally treated at 400°C, 500°C, 600°C, 700°C, 700°C, 800°C, 850°C, 900°C and 1000°C for 2 hours. The catalysts were characterised using nitrogen adsorption, mercury intrusion porosimetry (MIP), Raman spectroscopy and ammonia temperature programmed desorption.

The thermal sintered catalysts show first of all a decreasing BET surface area with sintering commencing between 700°C and 800°C when it decreases from the initial 71 m²/g to 62 m²/g and at 1000°C there is a mere 5 m²/g of surface area left. During sintering, the micro and meso-porosity is reduced as evidenced by MIP and depicted in figure 1.

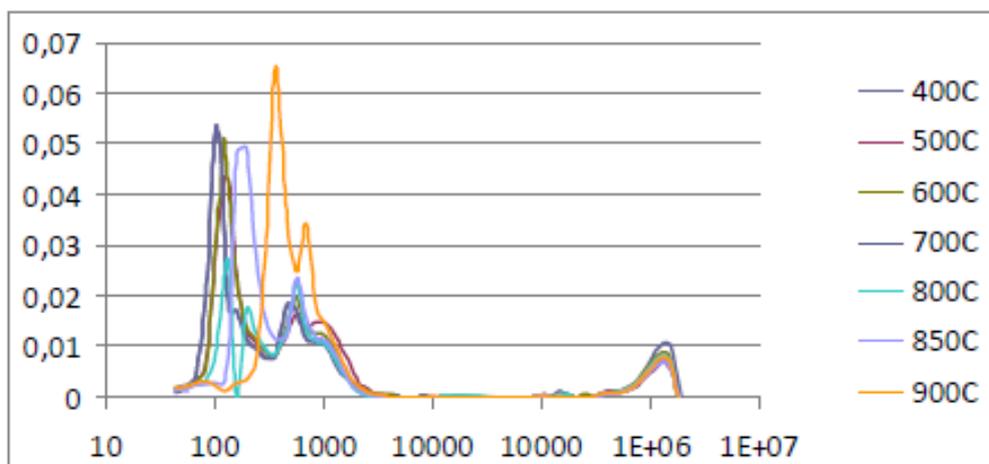


Figure 1 Incremental pore volume measured by MIP as a function of pore diameter (Å).

As may be seen in the figure, sintering decrease the amount of pores below and around 100 Å is reduced at a sintering temperature of 800°C and above. The most suitable catalyst based on the MIP appears to be the one sintered at 850°C which is further strengthened by the Raman analysis. There is a clear shift in the tungsten structure from monoclinic to triclinic between 850°C and 900°C and it is believed that the monoclinic phase is important for activity and selectivity. Further, the heat treatment shows that there is an increase in catalyst acidity measured as mmol NH₃/(m²/g) but a decrease in the acid strength as evidenced by a decrease in the desorption peak maximum temperature.

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