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Synthesis of enhanced catalytic materials in supercritical CO₂

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Synthesis of Enhanced Catalytic Materials in Supercritical CO₂

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the decision by the College of Deans.

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Tuesday 26 May 2020 at 9.00 hours

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Dedicated to my beloved family.

谨以此书献给我挚爱的家人

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Introduction

Aim and scope of this thesis

In recent years, nanostructured oxides have been increasingly applied in catalysis owing to their distinguished physicochemical properties compared to their bulk form, such as a large fraction of coordinately unsaturated sites on their surface and a high surface area. However, materials with special physicochemical features and unusual morphologies to promote a target reaction are still difficult to access by traditional synthetic routes, thus calling for exploring novel preparative approaches for enhanced nanostructured oxides. In addition, from the point of view of sustainable development, the synthesis of these materials should be carried out employing green methods. In this context, the synthesis and processing of nanostructured oxides in supercritical CO₂ (scCO₂) have attracted considerable attention. The use of scCO₂ as a solvent is a promising strategy: on the one hand, it displays exceptional properties as reaction medium, such as gas-like diffusivity and a tunable density that is intermediate between that of a gas and a liquid. Simply adjusting the temperature and pressure of CO₂ enables the examination of different synthetic environments. After the synthesis, CO₂ can be directly removed from the reaction mixture upon depressurisation. On the other hand, CO₂ is a readily available, non-toxic and inexpensive compound with a relatively easily accessible supercritical point, thus making scCO₂-assisted methods not only easy and low cost but also sustainable and green from the emission of excessive CO₂ point of view. A review of the studies on the synthesis of nanostructured oxide materials via scCO₂-assisted sol-gel or precipitation methods and their catalytic applications is presented in **Chapter 1**. This Ph. D. thesis presents the results of the investigation of novel nanostructured heterogeneous catalysts prepared by scCO₂-assisted sol-gel or precipitation methods and their application in reactions that are relevant in the context of green chemistry, such as oxidation reactions with H₂O₂ as environmentally friendly oxidant and conversion of bio-based materials into valuable chemicals. The green aspects of the performed reactions include the low reaction temperature, low catalyst loading, short reaction time and employment of green solvents. Here below, an elaborated outline of the four experimental chapters is provided:

Chapter 2

This chapter presents the synthesis of $\text{WO}_3\text{-SiO}_2$ materials with a scCO_2 -assisted sol-gel method and their application as a heterogeneous catalyst in the epoxidation of cyclooctene with H_2O_2 as green oxidant. The concentration of silicon precursor and the amount of basic solution in the scCO_2 -assisted synthesis were optimised with the aim of achieving good synthetic yield and catalytic activity of $\text{WO}_3\text{-SiO}_2$ materials. The leaching and recycling of the optimum catalyst were also studied under the optimum reaction conditions, which were searched by varying reaction solvent and type of H_2O_2 . The catalysts were thoroughly characterised to correlate their catalytic performance to their physicochemical properties. Additionally, the optimum catalyst was tested in the epoxidation of cyclohexene and limonene.

Chapter 3

The purpose of this chapter was to develop a scCO_2 -assisted precipitation method for the synthesis of Nb_2O_5 catalyst towards the oxidative coupling of aniline with H_2O_2 as environmentally friendly oxidant to produce azoxybenzene. The synthesised Nb_2O_5 revealed nanoparticulate morphology, which displays superior catalytic performance under mild reaction conditions, largely surpassing those of any other reported heterogeneous catalyst for this reaction and that of a reference catalyst prepared without scCO_2 , which could be related to its physicochemical properties as characterised by different techniques. With the purpose of further enhancing the yield of azoxybenzene, the other reaction conditions, such as reaction solvent, amount and type of H_2O_2 , were optimised, after which the leaching and recycling of the optimum catalyst are evaluated. The reaction mechanism based on the Nb_2O_5 catalyst was studied by conducting a catalytic test in the presence of a radical scavenger. The variety of the catalyst was examined by applying this catalyst in the oxidation of substituted anilines.

Chapter 4

A series of Nb_2O_5 materials were prepared with a scCO_2 -assisted precipitation method using different synthetic parameters, including the co-solvent and CO_2 pressure of scCO_2 -assisted precipitation process and the temperature of following thermal treatment. The catalytic activities of these Nb_2O_5 materials in the conversion of glucose to produce 5-hydroxymethyl-furfural (5-HMF) were studied and the activity of the optimum catalyst was compared to that of a reference Nb_2O_5 catalyst prepared without scCO_2 . Their activity difference was analysed based on the difference in their structural and acidic properties. The reaction temperature and ratio between catalyst and glucose were further optimised with the aim of enhancing the

productivity of the 5-HMF. The leaching and recycling of the optimum catalyst were also studied. Additionally, the catalytic performance of the optimum catalyst in the production of 5-HMF from different carbohydrates was investigated.

Chapter 5

Nb₂O₅ nanoparticles synthesised by a scCO₂-assisted precipitation method was applied in the conversion of dihydroxyacetone (DHA) to produce lactic acid, displaying good conversion of DHA, whereas its catalytic activity in converting pyruvaldehyde (intermediate product) prevents it from achieving high lactic acid yield within a short reaction time. On this backdrop, we designed a binary catalytic system, in which the sequential steps could be catalysed by Nb₂O₅ and a second catalyst. Detailed characterisation study allowed the understanding of the relation between the superior catalytic performance of the optimum combination of catalysts (Nb₂O₅ and Al₂O₃) to their physicochemical properties. Notably, the optimum catalytic system was tested in both batch and fixed-bed set-ups, in both of which different reaction conditions were optimised. The leaching and recycling in the batch set-up and the stability in the fixed-bed set-up of the optimum catalytic system were also studied.

Chapter 6

The last chapter provides a summary of the main achievements of this Ph. D. thesis on the topic of synthesising enhanced catalytic materials in supercritical CO₂.