A hybrid QM/MM embedded cluster approach to modelling the reactivity of carbon dioxide over metal oxide surfaces

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The reactivity of carbon dioxide over MgO, ZnO and zirconia (ZrO_2) surfaces is calculated using a hybrid quantum mechanical / molecular mechanical (QM/MM) embedded cluster approach[1,2] (see Figure 1). We have investigated the adsorption of CO_2 over an MgO(001) surface[3] and suggest the formation of both monodentate and tridentate carbonate is favourable, with the former being of lower energy. We also find that chemisorption at oxygen vacancy sites with a single localised electron could provide a route for the conversion of CO_2 to other products as upon adsorption the carbon atom is found to be exposed and therefore accessible to further reactants. The active site is common to a number of metal oxides, notably ZnO, which catalyses conversion of syngas ($CO/CO_2/H_2$) to methanol[2]. MgO would also support the conversion of CO_2 to methanol, however methane is a more favourable product. The fundamentals of CO_2 interactions with metal oxide surfaces are further probed on yttrium-stabilised zirconia over Brønsted and Lewis acid and base sites.

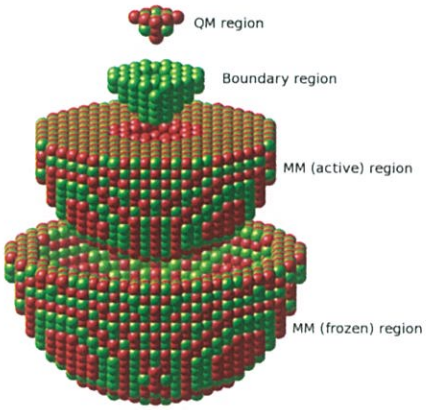

Figure 1. A graphic showing the hybrid QM/MM embedded cluster configuration – active and "frozen" MM regions surround a QM region. The boundary region is formed only of cations modelled with effective core potentials (ECP)

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Influence of the ionic liquid cation on the electrochemical reduction of CO_2

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The Electrochemical Reduction of Carbon dioxide (ERC) to valuable products could be an interesting strategy for CO_2 remediation. Products such as carbon monoxide, formic acid, oxalate and some hydrogenocarbons can be formed depending on the electrode material[1]. However, in these media, the ERC presents several limitations. Large overpotentials need to be applied to reduce the stable molecule of CO_2. Moreover, the Hydrogen Evolution Reaction (HER) is also encountered in aqueous media at potentials at which ERC is observed, decreasing the faradaic efficiency of the CO_2 conversion. The research of electrocatalysts is therefore essential for an efficient ERC.

Nowadays, traditional solvents can be successfully replaced by Room Temperature Ionic Liquids (RTILs)[2]. The number of publications considering the ERC in imidazolium based ionic liquids has been considerably increased these last years. It has been shown that these ionic liquids allow to promote the ERC. In 2012, the group of Masel published their results for the study of the reaction in [BMIm][BF_4]/ H_2O at silver electrode[3]. In this system, carbon monoxide is produced at very low overpotential and with an excellent faradaic efficiency. The formation of a complex between the imidazolium cation and the carbon dioxide adsorbed at the electrode surface is proposed to explain the electrochemical activity towards ERC. However, the mechanism of this reaction in imidazolium based ionic liquids is not completely understood. Moreover, little is known about the influence of other cations, such as tetraalkylammonium or pyrrolidinium based ionic liquids for ERC.

We are currently studying the influence of ionic liquid composition on the electrocatalytical performances of ERC by using of RTILs composed of different cations such as imidazolium, ammonium and pyrrolidinium and the same anion (bis(trifluoromethanesulfonyl)imide [NTf_2]), known to solubilize fairly large amounts of CO_2. The electrochemical behavior of CO_2 in these ionic liquids is studied by voltammetric techniques at a gold electrode. In imidazolium based ionic liquid, the ERC is observed at the same range of potential as the reduction of the imidazolium cation. Therefore, NMR spectroscopy is used for studying the electrochemical stability and reactivity of this ionic liquid at polarization where the ERC takes place. The reaction products of ERC are detected by gaseous and liquid chromatography techniques and compared in the different ionic liquids.

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Multivariate models for ionic liquids catalytic systems in CO_2 cycloaddition to propylene oxide

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Ionic liquids (IL) are known as good CO_2 sorbents and have been used as catalysts in reactions for CO_2 chemical conversion, such as cycloaddition to epoxy rings. To improve the catalytic system performance, and thus the utilization of CO_2, we must know how to change the reactions conditions and choosing the appropriate catalyst in pursuant with their properties. In this work a multivariate model was created with the aim of predicting catalytic system performance. The collected data were retrieved from our group's previous works[1]. The catalytic systems were composed of 1-*n*-butyl-3-methylimidazolium ionic liquids with different anions and Lewis-acids as cocatalysts. To select the variables that better represent the system an exploratory data analysis was performed[2], using principal component analysis (PCA) as an iterative process until obtaining all patterns and underlying data features. A Partial Least Squares Regression[3] (PLS-R) was also conducted, which is a robust statistical technique that allows to build a model for the maximum correlation between the predictor variables and the response. The desired responses to be modelled were carbonate yield and turnover number (TON). The conditions assessed were reaction time, CO_2 pressure, reaction temperature and the presence or absence of cocatalyst. The IL properties that were evaluated were thermal and transport properties and the CO_2 solubility at given pressure at reactional time zero. The exploratory analysis step showed the multivariate aspect of the data, with majority of the variables correlated with the catalyst efficiency. The presence of the cocatalyst $ZnBr_2$ is crucial for the majority of the reactions, CO_2 solubility at time zero was contrary to carbonate yield with this effect decreasing for heavier ILs. Other patterns were also founded relating reaction overall yields with ILs anion-cation interaction and thermophysical data. PLS-R resulted in one model for Yield, as a function of IL properties, and other related to reactional conditions, the first one with r^2 of 0.7609, and the latter with 0.87. For TON, one model dependent of the IL properties was created, with r^2 of 0.78.

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Direct synthesis of cyclic carbonate from alkenes

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Cyclic carbonates are considered as compounds of high importance, since they show promise in a number of different applications . They can be used as a components in lithium ion batteries, substrates for small molecule synthesis, additives, plasticizers or as an excellent aprotic polar solvents (replacements for DMF, DMSO) [1,2]. Furthermore, production of cyclic carbonates is one of the most promising technologies for chemical fixation and utilization of CO_2 [2]. In most of the reported work, researchers represent synthesis of carbonates from epoxides [3]. In this work, we present a direct route for the synthesis of cyclic carbonate starting from terminal alkene, which avoids the preliminary synthesis and isolation of terminal epoxide. Overall reaction consists of two steps: epoxidation of alkenes followed by CO_2 insertion into epoxide. Earlier reports show that 1%Au/ G catalyst has been reported active for epoxidation of alkenes [4], therefore, we performed epoxidation using Au supported catalysts. Different preparation methods were tested, and catalyst prepared by the sol-immobilisation exhibited the highest activity in the reaction (Figure 1).

For one-pot synthesis of cyclic carbonate from terminal alkene, a catalyst system consisting of Au/support and quaternary ammonium salt, has been applied, using O_2 as primary oxidant, and CO_2 in sequestration reaction. The influence of various reaction parameters, such as CO_2 pressure, reaction temperature, reaction time, and catalyst mass, has been studied in details. It should be noted that using this reaction strategy there is no need for an organic solvent, a high reaction temperature, or high CO_2 pressure.

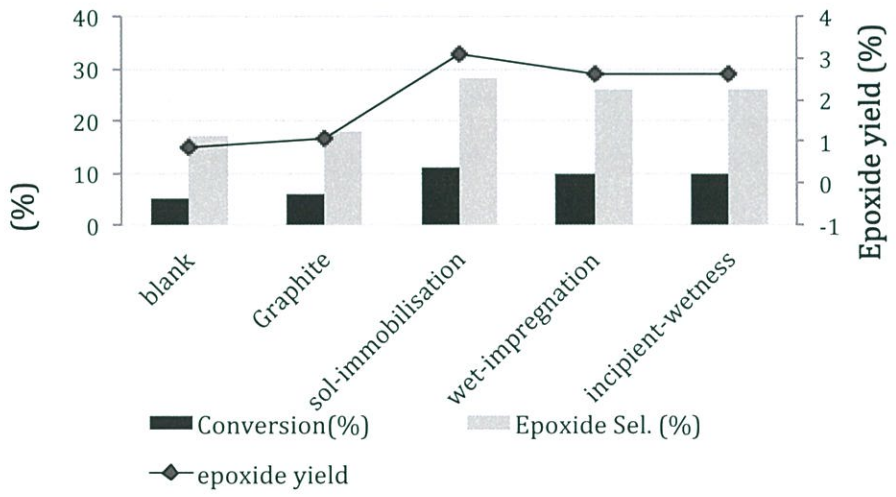

Figure 1: Epoxidation of 1-decene using Au/G catalysts: investigation into catalyst preparation method

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Synthesis of cyclic carbonates catalysed by aluminium heteroscorpionate complexes

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In the last two centuries, atmospheric carbon dioxide levels have largely increased every year due to the utilisation of fossil fuels.[1] Therefore carbon dioxide is potentially an abundant, economical and sustainable feedstock for the chemicals industry. In the last few decades much research has been directed towards the use of carbon dioxide as a chemical feedstock.[1] The production of cyclic carbonates from epoxides is one of the main industrial processes which uses carbon dioxide as a starting material, catalysed by relatively inefficient quaternary ammonium or phosphonium salts at high temperature and pressure. Cyclic carbonates have important applications as electrolytes in lithium–ion batteries, polar aprotic solvents and as chemical intermediates in organic synthesis.

In this contribution we report scorpionate-based aluminium complexes as highly efficient catalysts for the synthesis of cyclic carbonates from both monosubstituted and internal epoxides and carbon dioxide.[2] Trimetallic complex **1** had excellent catalytic activity towards terminal epoxides at one bar carbon dioxide pressure and room temperature whilst the bimetallic scorpionate complex **2** displayed a broader substrate scope catalysing the synthesis of cyclic carbonates from terminal and internal epoxides. A kinetic study has been carried out and based on this, a catalytic cycle has been proposed.

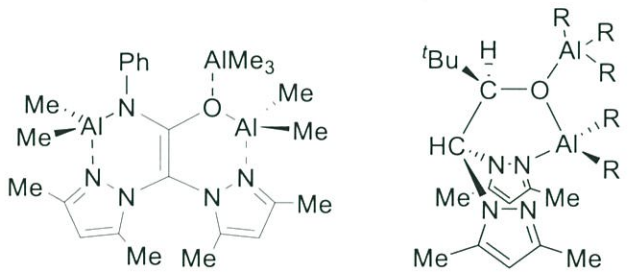

Figure 1. Aluminium(scorpionate) complexes for the synthesis of cyclic carbonates

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Understanding the potential of carbon dioxide utilization

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There has been a long held belief that there is an inherent problem with carbon dioxide utilization (CDU) in that it cannot meet the high volume demands required for CO_2 mitigation. It is certainly true that the quantities of CO_2 emitted in power production and heavy industry are huge. But can one technology alone deal with these emissions? Carbon Capture & Storage (CCS) has been proposed as an option but this treats CO_2 as a waste and so attracts disposal costs. Emitters need to develop new low cost technologies to reduce current parasitic energy losses. One option is to use the emitted CO_2 for enhanced hydrocarbon recovery (EHR) such as EOR (oil) or EGR (gas). So how much CO_2 can EHR sequester and how much hydrocarbon can be recovered?

This paper will consider the suite of technologies that make up CCUS. The global capacity at the current time for CCS will be considered and scenarios developed to predict capacity in 2030. Comparison to global CO_2 emissions show that there is a market demand for complimentary technologies such as EHR and CDU. This will be put in the context of global markets for fuels and chemicals up to 2030 and the availability of renewable energy. The aim is to show that CDU can act as an energy vectoring technologies at a scale that is comparable to and complimentary with CCS and EHR that rather than replacing these technologies will actually enhance capabilities. The results of these scenario models will be used to help influence European strategy through our interaction with the SCOT research programme (www.scotproject.org).

Improved solid oxide electrolysis for CO_2 conversion, using microchanneled cathode supports

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High temperature CO_2 electrolysis *via* solid oxide electrolysis cells (SOEC) is an effective way to convert CO_2 to CO, which is the first step to producing liquid fuels or chemicals. However, two main limitations currently hinder the commercial deployment of this technology: long term degradation of cell performance due to cathode oxidation, and catalyst deactivation due to carbon deposition. Ni based cathodes are considered to be the most promising materials for practical applications. However, with these, addition of H_2 or CO to the feed gas is required for the operation to avoid Ni oxidation [1].

Based on a novel oxygen transport membrane with a microchanneled structure, we previously showed the performance of a microchanneled anode support for solid oxide fuel cells (SOFC) with fast gas diffusion in the supporting anode [2]. In this study, we demonstrate a novel microchanneled cathode support for carrying out CO_2 reduction without the requirement of H_2 or CO in the feed gas. As shown Figure 1, through these channels, catalyst solution can readily be delivered to the interface between the cathode and electrolyte, where CO_2 reduction occurs. The catalyst is designed to both catalyse CO_2 reactions and also prevent Ni oxidation and carbon formation [3]. Moreover, the reactant gas CO_2 and product CO can be quickly transported through the channels. The fast CO diffusion avoids CO accumulation at the interface, which otherwise incurs carbon formation *via* the reaction of $2CO \rightarrow CO_2 + C$. As a result, CO_2 electrolysis with this arrangement using pure CO_2 has been successfully operated in long term tests (300 hours) with acceptable degradation compared to operation using the mixture of CO_2 and CO or H_2 in conventional SOECs. Such long term operation in pure CO_2 represents a significant breakthrough for commercial operation.

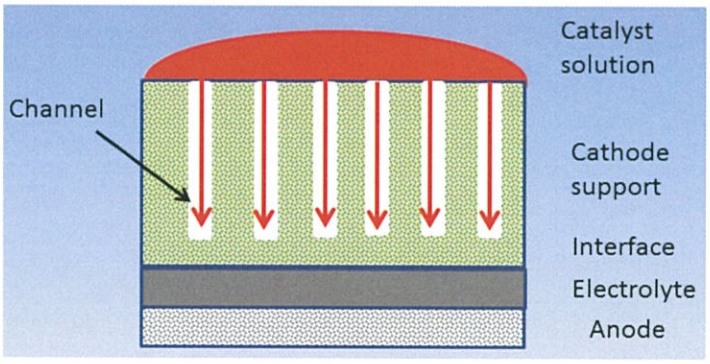

Figure1.Delivery of catalyst solution through channels to the interface of cathode support and electrolyte

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Carbon dioxide utilisation for methanol fuel production: Life cycle analysis

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Capturing carbon dioxide from flue gases and utilising it for the production of synthetic fuels, is a technology that aims to lessen environmental impacts caused by greenhouse emissions and contribute to restoring the carbon balance by recycling CO_2 from anthropogenic. Understanding the life cycle of supply chains for CCU (Carbon Capture and Utilisation) and how to improve its environmental performance is fundamental to moving these processes to industrial scale. A first step towards finding a sustainable supply chain is to detect carbon hotspots and find alternatives to reduce emissions in these areas. The aim of the research is to analyse two CCU processes with an LCA (Life cycle analysis) approach in a cradle to gate analysis.

BCM1: Tri-reforming coupling is a direct flue gas utilisation method where flue gas is mixed with methane to produce syngas that can then be synthetized into methanol.

BCM2: Catalytic hydrogenation for the production of methanol. The process includes a CO_2 capture stage using an absorption column with monoethanolamine. The CO_2 captured along with hydrogen obtained from electrolysis are then synthetized to methanol.

The two processes were modelled under same operating conditions and with a functional unit of 1t of methanol. Aspen plus and Gabi software were used for process modelling and for LCA work. Results show that energy consumption is greater for BCM2 and is attributed to hydrogen production and CO_2 compression units. BCM1 showed higher water consumption rates than BCM2, with cooling of syngas being the most water demanding. LCA results link BCM2 with overall higher environmental impacts.

Alternatives to the processes must be modelled to reduce energy penalties and environmental impacts. Preliminary results favour the use of direct use of flue gas versus a CO_2 capture stage, however changes such as water recycling and use of renewables still need to be considered.

Challenges for solar fuel production via potocatalysis

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Photocatalytic reduction of CO_2 for the production of solar fuels is a potentially highly efficient solar energy storage option and exciting utilization option. Currently, the development of photocatalysts for CO_2 reduction is limited by low efficiency. Challenges comparing improvements across the research field are caused by diversity in the current conversion reporting. This is partly due to a wide range of parameters used for reporting catalyst performance that may lead to confusion over conversion results and the intersecting requirements of this process. In the investigation of an optimized material, the complexities of the overall process may limit insights.

To tailor product formation and selection from photoreduction of CO_2 and give an introduction into the current challenges in the field, review of the photocatalytic process and complexities available will be discussed. This will provide information about flue gas and processing, reactor designs and illumination, product measurement, final products and separation for solar fuel production. This overview should improve the understanding of the various opportunities and entry points into the field.

Photoautotrophic carbon uptake by microalgae for biotransformations

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Photoautotrophs rely on light for energy to fix atmospheric carbon dioxide. This is a natural phenomenon that has evolved over the years to accommodate naturally available levels of light and nutrients, including carbon dioxide. It can, in principle, be utilised effectively for the development of biochemical processes that are carbon neutral and environmentally sustainable. A better understanding of this natural phenomenon would help us in developing improved biomimetic systems for sustainable utilisation of carbon dioxide and its conversion to products of commercial value. Our interest is in studying the carbon dioxide uptake by one group of photoautotrophs (microalgae) in a controlled reactor environment. Microalgae are a versatile group of photoautotrophic microorganisms that have high metabolic diversity and the potential to route the fixed carbon to organic carbon of high value or bulk biofuel precursors, such as lipids. Carbon dioxide uptake by this group of organism is dependent on the interplay between chemical and biological equilibrium of dissolved carbon in the medium the organism is exposed to. We will discuss our recent observations on the kinetics of carbon dissolution and its uptake by selected microalgae and what this implies to the application of this group of photoautotrophs for CDU, or indeed for the development of biomimetic systems based on this natural phenomenon.

CO_2 biorefinery model: A Sustainable biosequestration strategy with simultaneous energy and value addition

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Atmospheric CO_2 emissions pose significant impact on the global warming which needs a great deal of attention. Conventionally various methods exist to sequester CO_2 which basically does the capturing and storage. CO_2 has the potential to generate wide range of products, as it is a precursor for various chemicals/organic acid synthesis. Considering the potential of CO_2 and the huge demand for the synthesis of value added chemicals, current research is focused on utilizing CO_2 as substrate for chemicals production via various routes, in which bio-electro catalyzed reduction is one. However, there exists a need to create a sustainable CO_2 biosequestration strategy to synthesize value added products with simultaneous bioenergy generation. In this context, a biorefinery approach is described in which CO_2 is utilized/reduced by diverse bacteria as biocatalysts towards value added chemicals. A closed loop biorefinery model is investigated in our lab, which illustrates the bio-electrochemical reduction of atmospheric/industrial CO_2 to value added organic acids/volatile fatty acids (VFA) synthesis in bio-electrochemical systems (BES) (Fig.1). This VFA can be used as a feedstock for microalgal cultivation and biodiesel extraction. The deoiled algal cake resulting from the aforementioned process can be further utilized as a carbon source for acidogenic fermentation towards VFA, bio-hydrogen and CO_2 production. CO_2 and VFA can be utilized by photosynthetic bacteria for bioplastics, bioelectricity and bio-hydrogen production. In addition, artificial photosynthesis (SAP) process also utilizes CO_2 for carbohydrate synthesis, which can be further used in the anode chamber of BES. The present study provides a futuristic platform that breathes new life to cleaner atmosphere with sustainable biosequesteration of CO_2 for multiple value added products viz., VFAs, bioelectricity, bio-hydrogen, oxygen, bioplastics, biodiesel and carbohydrates synthesis.

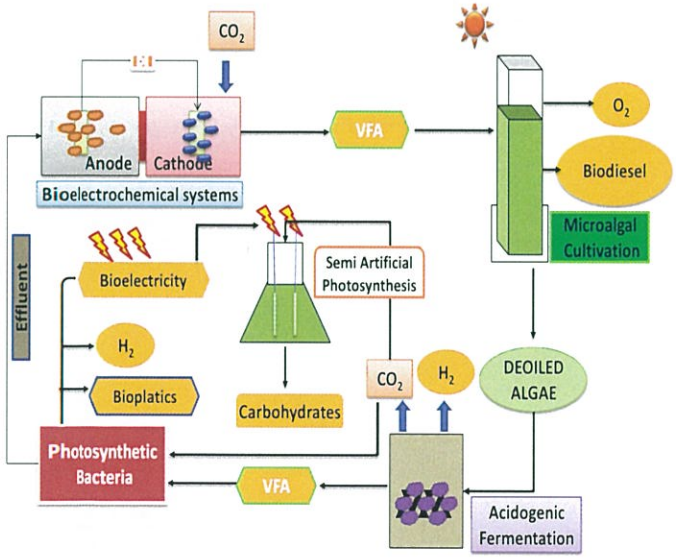

Fig.1 A closed loop biorefinery model for multiple products synthesis from CO_2

Size controlled formation of PdZn nanoparticulate for CO_2 hydrogenation

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We have investigated CO_2 hydrogenation on Pd/ZnO catalysts for methanol production. We observe a variation of the reaction pathway from reverse water gas shift (RWGS) reaction to CO_2 hydrogenation as the catalyst composition changes from Pd/ZnO into PdZn/ZnO. The activity towards methanol formation is largely influenced by the formation of PdZn bimetallic phases and these form under a reductive environment. Incorporation of Zn into Pd increases with the reduction temperature, but which also increases the particle size. Here we study PdZn formation from Pd/ZnO catalysts prepared by both incipient wetness impregnation and sol-immobilisation methods using PVA as stabiliser. Incipient wetness produced Pd nanoparticles of ~12.1 nm diameter (Fig. 1 Left). Sol immobilised catalysts produced a controlled size Pd with mean particle size of 3.1 nm (Fig. 1 Right). The sol-immobilised catalysts resulted in PdZn crystallites of around 5.7 - 12.1 nm upon reduction up to 700°C. In contrast, impregnation catalysts produced PdZn with a wide range of crystallite sizes from 7-60 nm when the Pd/ZnO catalyst was treated at similar reduction temperatures. We believe that by controlling the size of palladium, we will be able to control the growth of PdZn alloy. The influence of PdZn size on the CO_2 hydrogenation activity is shown in Fig. 2. Sol immobilised Pd/ZnO catalysts shows high conversion to methanol (Fig 2 Left). Catalysts by impregnation shows high CO_2 conversion towards CO with ~ 99% of selectivity. At reduction temperature of 700°C, the activity drops to only 2% of conversion as a result of large PdZn size (61 nm) produced. A high degree of interfacial contact between Pd metal and ZnO support is important for high methanol selectivity.

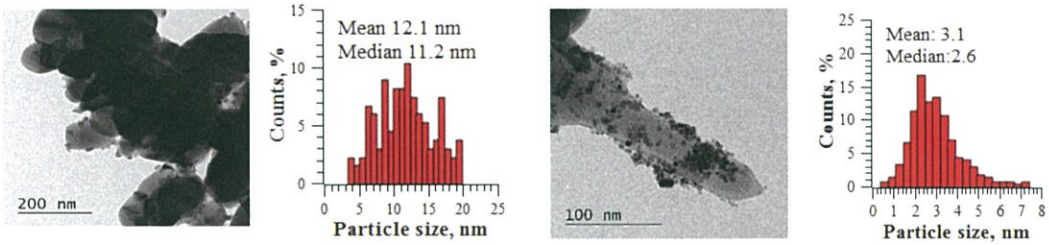

Fig 1: The TEM images and histogram of Pd distribution of 5% PdZnO catalysts prepared by impregnation method (Left) and sol immobilisation method (Right)

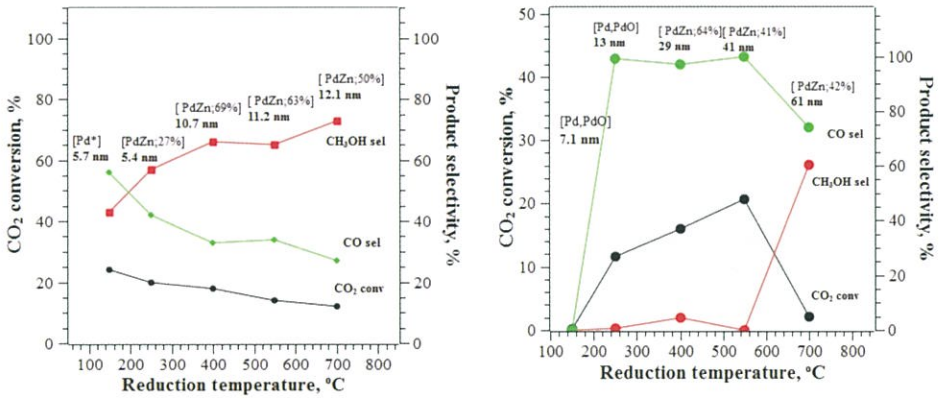

Fig 2: Influence of H_2 reduction treatment on 5 % Pd ZnO catalysts prepared by sol immobilisation method (Left) and impregnation method (Right). The activity of the catalysts was tested on CO_2 hydrogenation reaction at 30 ml/min of 3 H_2:1 CO_2 gas mixture, 20 bar and 250°C.

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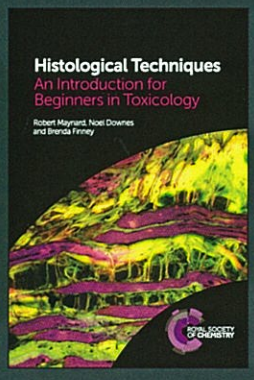

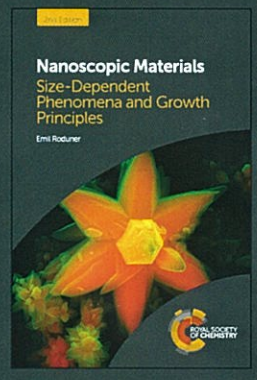

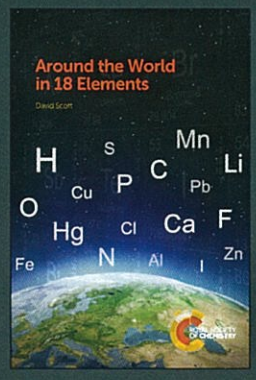

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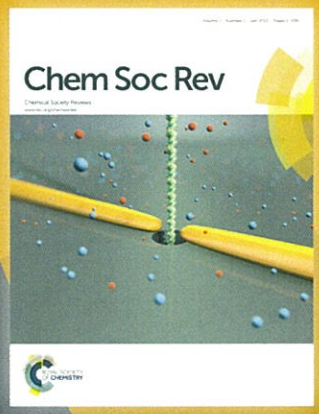

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