Nanocatalysts from Ionic Liquid Precursors for the Direct Conversion of CO_2 to Hydrocarbons

Zara Shiels[1,2*], John Harrison[2], Peter Nockemann[1] and Nancy Artioli[1]
[1] *School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast (UK)*
[2]*Renewable Engine, South West College, Cookstown (UK)*
*zshiels02@qub.ac.uk

Introduction

The direct conversion of carbon dioxide (CO_2) into lower olefins (C_2-C_4) is a highly desirable process as a sustainable production route. Lower olefins, i.e., ethylene, propylene and butenes (C_2-C_4), are key building blocks in the current chemical industry. The reaction proceeds *via* two main consecutive reactions: Reverse Water Gas Shift (RWGS) to produce CO followed by the further conversion of CO to hydrocarbons *via* the Fischer−Tropsch reaction[2]. This process is achieved by a multifunctional iron-based catalyst supported on zeolites providing three types of active sites (Fe_3O_4, Fe_5C_2 and acid sites), which cooperatively catalyse a tandem reaction[1].
To date, attempts at synthesising a suitable catalyst for the direct hydrogenation reaction follow a conventional precipitation procedure, whereby Iron Oxide Nanoparticles (*ION*s) are produced and then embedded within a zeolite structure by granule mixing. This method provides limited control over the size and shape of the IONs formed; a characteristic of imperative importance due to its significant effect on the hydrocarbon product distribution obtained. In our novel approach, ionic liquids are utilised for the synthesis of the *ION*s resulting in better control over size and morphology of the nanostructured material, and as a consequence, better conversion and selectivity towards the olefins.

Materials and Methods

Na–Fe_3O_4 nanocatalysts obtained by a one-pot synthesis method, already demonstrated in literature[2], employed a precipitation method (**PM**) involving a mixture of iron (II) and iron (III) chloride hydrate, deionised water and HCl to result in a clear solution. Subsequently, NaOH has been added as a precipitating agent, which resulted in the formation of a black precipitate, which consisted of magnetite, Fe_3O_4 (**PM-Na**). To prepare an Fe_3O_4 sample without sodium, ammonium hydroxide was used as the precipitating agent. These samples were then used as a benchmark for the following novel method. An ionic liquid-assisted synthesis method consisted of heating two iron precursors of Fe (II) and Fe (III) chloride hydrates in a reaction medium of [C_4mim][OAc] ionic liquid (**IL**). After the synthesis, the Fe_3O_4 particle were embedded in either HZSM-5 (SiO_2/Al_2O_3 = 300) or HZSM-5 (SiO_2/Al_2O_3 = 80) zeolite by either granular mixing or mixing in a ball mill at a mass ratio of the two components of 1:1.
CO_2 hydrogenation reactions were performed at 320 °C, 25 bar and a H/CO_2 ratio of 3:1, in a stainless steel fixed-bed reactor with an inner diameter of 15 mm. Typically, 0.75 g of catalyst Fe_3O_4/Zeolite was mixed with alumina (20–40 meshes) in a 1/1 mass ratio. Prior to reaction, the catalyst was reduced *in-situ* at 350 °C for 8 h in a pure H_2 flow at atmospheric pressure. All products from the reactor were analysed with an online gas chromatograph (GC) equipped with ShinCarbon and PONA columns.
The materials were characterized with ICP-OES (Agilent 5100 ICP-OES), PXRD (PANanalytical X'Pert Pro Diffractometer), TEM (G2 Talos) operated at 200 kV, H_2 Chemisorption (Micromeritics AutoChem II 2920).

Results and Discussion

The ionic-liquid assisted synthesis of a nanocrystalline magnetite precursor showed that ionic liquids provide a controlled precipitation method thanks to their dual functionality as solvent and templating agent. Characterization of the prepared catalysts with the IL method by PXRD shows high phase purity for magnetite, Fe_3O_4, small particle size and TEM shows good dispersion with the zeolite component. The compounds obtained by ionic liquid method result in amorphous XRD patterns before calcination, however, show phase purity and good crystallinity after calcination at 420° C under a flow of N_2. This has also been confirmed by SEM and TEM (Figure 1.a, b). Hydrogen temperature-programmed reduction (H_2-TPR) was used to determine the reducibility of the Fe_3O_4 and the hydrogen uptake.
Hydrogen temperature-programmed reduction (H_2-TPR) was used to determine the interaction between Fe species and the support. As shown in Figure 1.c, all the catalysts present two peaks with increasing reduction temperature, which are assigned to the conversions Fe_3O_4—FeO and FeO—Fe, respectively. It is observed that catalyst (**PM**) starts to be reduced at lower temperature compared to the catalyst (**IL**), indicating the interaction between iron oxides and the support is weaker in the first sample.

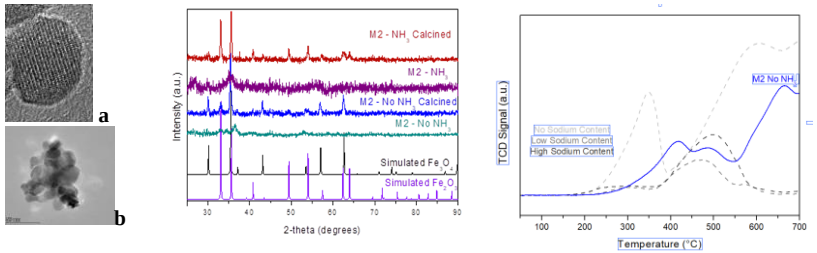

Figure 1 - TEM of catalysts synthesized by **PM-Na** (top) and **IL** (bottom), PXRD analysis of ionic liquid method (middle), TPR of ionic liquid method against precipitation method (right).

Significance

We report here on a novel methodology for the controlled synthesis of a Fe_3O_4/HZSM-5 multifunctional catalyst for the direct hydrogenation of CO_2 to gasoline. The product composition and selectivity can be tuned by the choice of by the choice of ionic liquid in the synthetic method and the Fe precursors. This study provides a new pathway for the synthesis of nanocatalysts to produce liquid fuels by utilising CO_2 and H_2, which may in the future lead to alternative approaches to overcome issues with the intermittency of storing and/or utilising energy from renewable sources (photovoltaics, wind energy).

References

[1]Y. Yuan, S. Huang, H. Wang, Y. Wang, J. Wang, J. Lv, Z. Li, and X. Ma, ChemCatChem 2017, 9, 3144 – 3152.
[2] J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun, Nat Comm, 2017, 8:15174, doi: 10.1038/ncomms15174.

List of Talks UKCC 2021

#	Title	Authors
Pl 01	Constructing and Modifying Indoline and Chromane Cores: A Catalytic Story	Anthony Burke
Pl 02	Mechanochemical and mechanocatalytic reactions in ball mills – from voodoo to science	Ferdi Schüth
Pl 03	Approaches to catalytic emissions control at low temperature	Todd Toops
Pl 04	Accelerating Catalyst Development Using Advanced 3D and in-situ Scanning Transmission Electron Microscopy	Sarah Haigh
K 01	Photocatalysis with plasmons: from light absorption to charge generation and utilization	Jacinto Sá
K 02	Kinetics, Modelling and Process Design of Hydrogen Production by Aqueous Phase Reforming of Polyols	Dmitry Murzin
K 03	Catalytic Cascade Reactions of Ethanol to Butanol and Butadiene over Metal Phosphate and Metal Oxide Catalysts	Robert J. Davis
K 04	Dual functional materials development for integrated CO_2 capture and conversion	Chunfei Wu
K 05	Catalytic materials under investigation through the eye of a spectroscopist	Silvia Bordiga
K 06	Fuels and chemicals from waste and low value co-products	James McGregor
K 07	Tailoring lamellar materials: a crucial key for enhancing their catalytic efficiency in the synthesis of fine chemicals	Octavian Pavel
K 08	Controlling Hydrogenation Rates in Aqueous Environments via Applied Potential and Brønsted Acidity	Oliver Gutierrez-Tinoco
K 09	Nano-structured multicomponent catalysts for gas-phase CO_2 conversion	Tomas Ramirez Reina
K 10	New Insights into Homogeneous Catalysis from operando FlowNMR spectroscopy	Ulrich Hintermair
K 11	Catalytic Valorisation of Lignin: Are We Nearly There Yet?	Gary Sheldrake

O 01	Design Cu based binary metal oxide system for cascade NH_3 oxidation	Xuze Guan and Ryan Wang
O 02	Utilization of CO_2 by converting into substituted urea using Sn-Ni oxide catalyst: Structure-activity correlation and mechanistic studies	Nagendra Kulal, Rajappan Vetrivel and Ganapati V. Shanbhag
O 03	Conversion of CO_2 to added value products via rWGS using Fe-promoted catalysts: Carbide or not carbide; that is the question	Qi Zhang, Laura Pastor-Pérez and Tomas Ramirez Reina
O 04	Nanocatalysts from Ionic Liquid Precursors for the Direct Conversion of CO_2 to Hydrocarbons	Zara Shiels, John Harrison, Peter Nockemann and Nancy Artioli
O 05	Insights on Ethene Oligomerization with Supported d8 Metal Atoms	Nicholas Jaegers, Konstantin Khivantsev, Libor Kovarik, Jian Zhi Hu, Yong Wang and Janos Szanyi
O 06	Precise identification and characterization of catalytically active sites on the surface of γ-alumina for alcohol dehydration	Konstantin Khivantsev, Nicholas R. Jaegers, Ja-Hun Kwak, Janos Szanyi and Libor Kovarik
O 07	Controlling Reaction Routes to Maximize the Rates of C-O bond Cleavage of Aryl Ethers on Metal Catalysts	Julian Schmid, Meng Wang, Oliver Gutierrez, Donald Camaioni and Johannes Lercher
O 08	In-situ NMR studies of aerobic oxidations over heterogeneous catalysts	Carmine D'Agostino, Mick D. Mantle and Lynn F. Gladden
O 09	Evolution of atomic site in oxidation chemistry	Ryan Wang
O 10	Ammonia Electro-Oxidation Using Pt Decorated Molybdenum Carbide Nanosphere	Maryam Bayati, Xiaoteng Liu, Keith Scott, Patricia Abellan and Michael Dixon
O 11	Role of catalyst pre-treatment in aqueous-phase reforming of glycerol to propylene glycol	Rajan Pandya and Chandrashekhar Vasant Rode
O 12	The structures of 1-propanol monomer and dimer species on Brønsted acid sites as key intermediates for dehydration in zeolites	Sungmin Kim, Mal-Soon Lee, John Fulton, Oliver Gutiérrez, Donald Camaioni, Roger Rousseau, Niri Govind, Thomas Huthwelker and Johannes Lercher
O 13	Continuous flow Curtius rearrangement coupled with an enzyme mediated purification strategy	Megan Smyth, Marcus Baumann, Thomas S. Moody and Scott Wharry
O 14	Graphene oxide catalysed N-Heterocyclization of Aniline Derivatives by Dihalides in aqueous media	Jyoti Ambre, Olviya Gonsalves and Parag Nemade
O 15	Smectitic Clays as Clean and Cost Effective Heterogeneous Catalysts	Oscar Kelly, Tom Lamont, Adam Mudashiru, Callum Morris, Pierre Chambon and Adam Brookbanks

O 16	Transition Metal Chalcogenide Bifunctional Catalysts for Chemical Recycling by Plastic Hydrocracking	Aleksander Tedstone
O 17	Catalyst development for carbon nanotubes production from waste plastics	Chunfei Wu, Su He and Xiaotong Liu
O 18	The Right Catalyst Carrier Selection	Rob Parry, Matteo Baraldi, Markus. M. Schubert
O 19	Supported oxygen evolution catalysts to lower precious metal loading and improved conductivity in proton exchange membrane water electrolyzers	Yagya Regmi
O 20	Electro-catalysis for Advanced Direct Ethanol Fuel Cells Using Higher Energy Liquid Oxygenates	Cheng Li and Wen-Feng Lin
O 21	Structure Sensitivity during the Electrocatalytic Hydrogenation and Oxidation of Biomass-Derived Molecules	Juan Lopez-Ruiz, Yang Qiu, Udishnu Sanyal, Katherine Koh, Oliver Gutierrez-Tinoco and Jamie Holladay
O 22	Multiscale imaging and in situ analysis of industrially relevant materials for emission control	Monik Panchal, Emma Gibson, Manfred Erwin Schuster, Timothy Hyde, Andrew Beale, Richard Catlow, Andrew York and Paul Collier
O 23	Carboxymethylation of Bio-alcohols with Dimethyl Carbonate: Effect of Morphology on the Catalytic Activity of CeO_2	Kempanna S. Kanakikodi, Nagendra Kulal, K.S. Subramanya, M. S. Puneethkumar, Ganapati V. Shanbhag and Sanjeev P. Maradur
O 24	Non-metallic Aerobic Oxidation of Alcohols over Anthraquinone-Based Compounds	Jingpeng Zhao, Dan Wu, Willinton Yesid Hernandez Enciso, Wen-Juan Zhou, Mickael Capron and Vitaly Ordomsky
O 25	Attenuation of dimethyl ether formation from the reaction of methanol over an alumina based methyl chloride synthesis catalyst	David Lennon
O 26	Solvation effect on Pd catalyzed C=O bond hydrogenation of benzaldehyde	Yue Liu, Guanhua Cheng, Andreas Jentys, Oliver Gutiérrez, Cathy Chin and Johannes Lercher
O 27	Development of the techniques of modification of carbon nanotubes to create a unique support for lipase B from Candida antarctica	Anna Szelwicka, Magdalena Sitko, Anna Wolny, Sławomir Boncel and Anna Chrobok
O 28	A computer aided synthesis planning tool for biocatalysis: RetroBioCat	William Finnigan, Lorna Hepworth, Sabine Flitsch and Nicholas Turner
O 29	New strategies for performing homogeneous catalysis and biocatalysis in water	Hasan Imam, Kyle Hill, Peter McNeice, Andrew Reid, Stefan Mix, Paul C J Kamer, Patricia Marr and Andrew C Marr
O 30	Valorization of bio-derived furfuryl alcohol to make furfuryl acetate over solid acid	S Sujith, B J Vaishnavi and Ganapati V Shanbhag

	catalysts: Effect of acidity and porosity on activity	
O 31	Selective Hydrogenolysis of Lignin-Derived Guaiacol under Ambient Hydrogen Pressure	Hui Zhou
O 32	CO Poisoning of Ru Catalyst in CO_2 Hydrogenation under Thermal and Plasma Conditions	Shanshan Xu, Sarayute Chansai, Xiaolei Fan and Chris Hardacre
O 33	Towards the Utilisation of CO_2: Ionic Liquid Sorbents and the Effect of Flue Gas Impurities	Adam Greer, Rebecca Taylor, Helen Daly, Johan Jacquemin, Richard Catlow, Chris Hardacre and Matthew Quesne
O 34	Nano structured Ru-Ni Catalysts for Selective Hydrogenation of Levulinic Acid to gamma-Valerolactone	Gayatri Kasar, P. N. Bhosale and Chandrashekhar Rode
O 35	Catalytic Hydrogenation of Methyl Linoleate using Pyrazolyl Nickel(II) and Palladium(II) Complexes as Catalysts	Oluwasegun Olaoye, Olayinka Oyetunji, Banothile Makhubela, Apollinaire Munyaneza, Gopendra Kumar and James Darkwa
O 36	Aqueous phase hydrogenolysis of glycerol to 1,3-propanediol over bifunctional catalyst comprising heteropolyacids and Pt	Mohammad Khan, Huanting Wang, Santosh J. Gharpure, Sanjay M. Mahajani and Akkihebbal K Suresh
O 37	Role of Supports in Pd Catalyzed Furfural Hydrogenation	Nandan Date, Rajeev Chikate and Chandrashekhar Rode
O 38	Novelty of Ru-DTP@MOF-5 as an active and efficient catalyst in one-pot synthesis of flavouring agent allyl 4-cyclohexanebutyrate	Dipti Wagh and Ganapati Yadav
O 39	The application of inelastic neutron scattering to investigate iron-based Fischer-Tropsch to olefins catalysis	Alisha Davidson, Emma Gibson, Giannantonio Cibin, Hendrik van Rensburg, Stewart Parker, Paul Webb and David Lennon
O 40	Structured Silicalite-1 Encapsulated Ni Catalyst Supported on SiC Foam for Dry Reforming of Methane	Huanhao Chen, Yibing Mu, Chris Hardacre and Xiaolei Fan
O 41	The superior hydrothermal stability of Pd/SSZ-39 in low temperature passive NO_x adsorption (PNA) and methane combustion	Konstantin Khivantsev, Nicholas R. Jaegers, Libor Kovarik, Meng Wang, Jian Zhi Hu, Yong Wang, Miroslaw Derewinski and Janos Szanyi
O 42	Pushing the limits of precious metal atom economy for three-way-catalysts (TWC): thermally stable and highly active single Rh atom catalysts (Rh1/ceria) for NO abatement	Konstantin Khivantsev, Nicholas R. Jaegers, Libor Kovarik, Jinshu Tian, Carlos Garcia Vargas, Janos Szanyi and Yong Wang
O 43	Identification of Ru/Ceria among single atom ceria catalysts as a stable and superior material for abatement of diesel and gasoline engine pollutants	Konstantin Khivantsev, Libor Kovarik, Nicholas R. Jaegers, Jinshu Tian, Xavier Periera Hernandez, Yong Wang and Janos Szanyi

O 44	Detection and characterization of super-electrophilic metal (Pd+2) cations in zeolite SSZ-13: novel chemistry for adsorption (vehicle emissions control) and catalysis applications	Konstantin Khivantsev, Nicholas R. Jaegers, Libor Kovarik, Mark Engelhard, Hristiyan A. Aleksandrov, Georgi N. Vayssilov, Yong Wang and Janos Szanyi
O 45	Synergy in Polyoxometalate-Stabilised Ruthenium Nanoparticle Catalysis	R. John Errington, Lan Feng, Simon Doherty, Julian Knight, Ye Wang, Lasheng Long and Rong Chen
O 46	High throughput XAS reactor system for operando spectroscopy study	Shaojun Xu, Giannantonio Cibin, Diego Gianolio, Veronica Celorrio, Stephen Parry, Emma K. Gibson and C. Richard A. Catlow
O 47	Operando Potassium K-edge X-ray Absorption Spectroscopy: Investigating Potassium Catalysts during Soot Oxidation	Simon Kondrat, Catherine Davies, Alex Mayer, Giannantonio Cibin, Volkan Degirmenci and Stan Golunski
O 48	Towards Determining Adsorbate Orientation on a Supported Pd Hydrogenation Catalyst via in-situ DRIFTS	Annelouise McCullagh, Emma Gibson and David Lennon
O 49	Understanding structure-function relationship in NH_3-SCO using combined spatially resolved operando techniques	Donato Decarolis, Peter Wells, Alexandre Goguet and Emma Gibson
O 50	Formation of active species over ZCuOH and Z2Cu sites in the Cu-CHA catalysts: Cu speciation in SCR reaction with operando XAS	Yiyun Liu, Ryan Wang and Loredana Mantarosie
O 51	Spectroelectrochemical Insights into the CO-Tolerance of Electrocatalysts Modified with Tungsten Oxide	Andy Wain, Tim Rosser, Douglas Stewart, Keith Scott, Edward Brightman, Donald Macphee and Mohamed Mamlouk
O 52	Operando Spectroscopy Kinetic Analysis of Methanol-to-Olefins Conversion over H-SAPO-34 and H-ZSM-5 Molecular Sieves	Leila Negahdar, Bert Weckhuysen and Andrew Beale
O 53	Catalytic reduction of CO by H_2 on the cobalt Co(111) surface	David Santos-Carballal and Nora H. de Leeuw
O 54	Identity of S-containing Species on Sulfated Zirconia Surface: Ab initio Investigation of Surface Properties and Pyrosulfate Formation	Maicon Delarmelina and Richard Catlow
O 55	Morphology of Cu Clusters Supported on Reconstructed Polar ZnO (0001) and (000$\bar{1}$) Surfaces	Michael Higham, David Mora-Fonz, Alexey Sokol, Scott Woodley and Richard Catlow
O 56	Influence of Topology and Brønsted Acid Site Presence on Methanol Diffusion in Zeolites Beta and MFI	Cecil Botchway, Richard Tia, Evans Adei, Alexander O'Malley, Nelson Dzade, Carlos Hernandez-Tamargo and Nora de Leeuw

O 57	Resolving deactivation pathways of Co porphyrin-based electrocatalysts for CO_2 reduction in aqueous medium	Yijiao Jiang
O 58	Catalyst design informed by product and process requirements	Mohammad Reza Abbasi, Federico Galvanin, John Blacker and Asterios Gavriilidis
O 59	Processing and analysing large quantities of data in catalysis science	Abraham Nieva de La Hidalga, Donato Decarolis, Shaojun Xu, Santhosh Matam, Willinton Yesid Hernández Enciso, Corinne Anyika, Brian Matthews and Narayanan Krishnan