

Nanocatalysts from Ionic Liquid Precursors for the Direct Conversion of CO₂ to Hydrocarbons

Callum Jeffrey¹, Peter Nockemann¹, Nancy Artioli^{1*}

¹ School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, UK

*corresponding author: n.artioli@qub.ac.uk

Introduction

The direct conversion of carbon dioxide (CO₂) into lower olefins (C₂-C₄) is a highly desirable process as a sustainable production route. Lower olefins, i.e., ethylene, propylene and butenes (C₂-C₄), 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 reaction². This process is achieved by a multifunctional iron-based catalyst supported on zeolites providing three types of active sites (Fe₃O₄, Fe₅C₂ and acid sites), which cooperatively catalyse a tandem reaction¹. To date, attempts at synthesising a suitable catalyst for the direct hydrogenation reaction follow a conventional precipitation procedure, whereby Iron Oxide Nanoparticles (IONs) are produced and then embedded within a zeolite structure by granule mixing. This method provides no 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 IONs 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-Fe₃O₄ nanocatalysts obtained by a one-pot synthesis method employing a precipitation method 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, Fe₃O₄. The compound was then characterised using IR, PXRD (see Fig. 1), SEM / EDX and TPR (Fig. 2). Depending on the amount of washing water, the catalyst contained varying amounts of residual sodium content of up to 7·10⁻² %.

The ionic liquid-assisted synthesis involved heating the reaction medium consisting of the ionic liquid 1-butyl-3-methyl imidazolium bistriflimide, [C₄mim][Tf₂N], oleic acid and iron pentacarbonyl under reflux. The precursor iron pentacarbonyl decomposed in a controlled manner by heating the sample up; CO is produced and the iron reacts with residual H₂O in the ionic liquid mixture to result in Fe₃O₄. Following decomposition, the produced magnetite nanoparticles are separated from the reaction medium through application of a neodymium magnet. The Na-Fe₃O₄/Zeolite catalyst was typically prepared by granule mixing Na-Fe₃O₄ catalysts prepared with the methods above with zeolites (HZSM(SiO₂/Al₂O₃ = 80 and 300) in a ball mill at a mass ratio of the two components of 1:1.

CO₂ hydrogenation reactions were performed at 320 °C, 3 MPa H₂/CO 3,3 in a stainless steel fixed-bed reactor with an inner diameter of 15 mm. Typically, 1 g of composite catalyst (20–40 meshes) with Na-Fe₃O₄/Zeolite 1/4 1/1 (mass ratio) was used. Prior to reaction, the catalyst was in-situ reduced at 350 °C for 8 h in a pure H₂ flow at atmospheric pressure.

All of the products from the reactor were introduced in a gaseous state and analysed with an online gas chromatograph (GC).

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. This level of control over the morphology of the produced IONs allows for the selectivity of the hydrocarbon distribution to be directly tailored to light olefin production. Characterization of the prepared catalysts by PXRD (Figure 1) shows phase purity for the magnetite obtained from the conventional precipitation method, and shows no alteration after granulation with the zeolite, showing the presence of high purity in Fe₃O₄, small particle size and good dispersion with the zeolite component. The compounds obtained by the ionic liquid methods result in much broader XRD patterns, pointing at less crystallinity and smaller particle size. This has also been confirmed by SEM and TEM. Hydrogen temperature-programmed reduction (H₂-TPR) was used to determine the interaction between Fe species and the support. As shown in Figure 2 for the HZSM 80, all the catalysts present two peaks with increasing reduction temperature, which are assigned to the conversions Fe₃O₄—FeO and FeO—Fe, respectively. It is observed that Fe₃O₄/HZSM80 start to be reduced at lower temperature compared to the catalyst with low (L) and high (H) Na content. This indicates the interaction between iron oxides and the support is weaker if Na is completely removed.

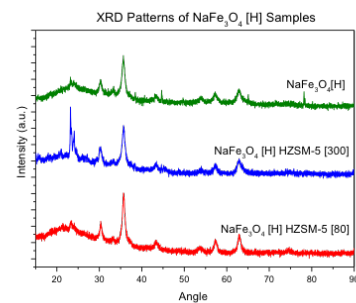


Figure 1. XRD patterns of Na-Fe₃O₄ sample with high Na content (H) and Na-Fe₃O₄ mixed with HZSM with SiO₂/Al₂O₃ = 80 and 300.

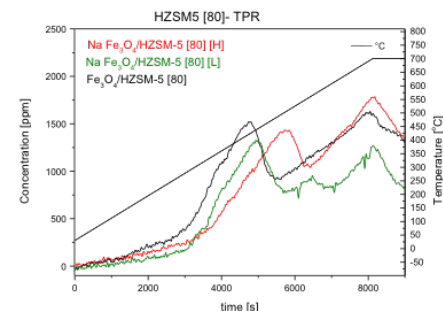


Figure 2. TPR profile of 4000 ppm H₂ in Ar from r.t. to 700°C, 5°C/min

Significance

We report here on a novel methodology for the controlled synthesis of a Na-Fe₃O₄/HZSM-5 multifunctional catalyst for the direct hydrogenation of CO₂ to gasoline. The catalytic testing under industrially relevant conditions resulted in improved selectivity to C₅-C₁₁ as well as low CH₄ and CO selectivity. Furthermore, the product composition can be tuned by the choice of zeolite type, and by the choice of ionic liquid in the synthetic method. This study provides a new pathway for the synthesis of nanocatalysts for the production of liquid fuels by utilising CO₂ and H₂, 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

- ¹Y. 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, DOI: 10.1038/ncomms15174

Columbus ABCDEF	Columbus GH	Columbus IJ	Columbus KL
2:30 PM Thu-CHAB-1430 High-Entropy Alloy Catalysts for Ammonia Decomposition. Pengfei Xie and Chao Wang , <i>Johns Hopkins University, USA</i> .	2:30 PM Thu-CHGH-1430 Ion-Exchange Promoted Hydrothermal Stability of Platinum Catalysts Supported on Layered Protonated Titanate Nanowire Arrays. Xingxu Lu ¹ , Wenxiang Tang ¹ , Shoucheng Du ¹ , Liaoyong Wen ¹ , Junfei Weng ¹ , Yong Ding ² , Steven Suib ¹ and Pu-Xian Gao ¹ , (1) <i>University of Connecticut, USA</i> , (2) <i>Georgia Institute of Technology, USA</i> .	2:30 PM Thu-CHIJ-1430 Selectivity Differences between Thermocatalytic and Electrocatalytic Hydrogenation of Biomass-Derived Oxygenates. Reda Bababrik , Daniel Resasco and Bin Wang , <i>University of Oklahoma, USA</i> .	2:30 PM Thu-CHKL-1430 Capturing the Restructuring of Co-Based Catalysts in Oxygenate-Driven Fischer-Tropsch Synthesis from First Principles. Greg Collinge ¹ , Renqin Zhang ¹ , Motahare Athariboroujeny ¹ , Trevor Wood ¹ , Kirill Shumilov ² , Anastassia Alexandrova ² , Norbert Kruse ¹ and Jean-Sabin McEwen ¹ , (1) <i>Washington State University, USA</i> , (2) <i>University of California, Los Angeles, USA</i> .
2:50 PM Thu-CHAB-1450 Bifunctional Metal-Acid Catalysis: Optimizing the Spatial Organization of Functional Components at Nanoscale. Kang Cheng ¹ , Zhaorong Zhang ² , Glenn J. Sunley ³ , Jovana Zečević ¹ and Krijn P. de Jong ¹ , (1) <i>Utrecht University, Netherlands</i> , (2) <i>BP Group Technology, USA</i> , (3) <i>BP Chemicals, United Kingdom</i> .	2:50 PM Thu-CHGH-1450 Selective Removal of CuO _x Spectator Species By Acid Treatment Minimizes N ₂ O Formation on Cu-SSZ-13. Dylan Trandal , Yadan Tang and Krishna Kamasudram , <i>Cummins Inc., USA</i> .	2:50 PM Thu-CHIJ-1450 Effect of Metal on the Electrochemical Reduction of Benzaldehyde. Jacob Anibal and Bingjun Xu , <i>University of Delaware, USA</i> .	2:50 PM Thu-CHKL-1450 Synergy Effect of Two Sets of Single-Atom Sites (Ni ₁ and Ru ₁) on Catalyst Surface for Reforming CH ₄ . Yu Tang ¹ , Ziyun Wang ² and Franklin Tao ¹ , (1) <i>The University of Kansas, USA</i> , (2) <i>The Queen's University, United Kingdom</i> .

3:10 PM – 3:40 PM: Coffee Break

3:40 PM – 5:20 PM: Oral Sessions

Columbus ABCDEF	Columbus GH	Columbus IJ	Columbus KL
Oxidation and Epoxidation Reactions	Catalysis with Nanoparticles II	H₂ Production, Biogas Processing, and Gasification	Environmental: Catalytic Oxidation IV
Session Chairs: Beata A. Kilos-Reaume , <i>The Dow Chemical Company, USA</i> and Jae Hyung Kim , <i>SABIC, USA</i> .	Session Chairs: Joshua Willis , <i>ExxonMobil Chemical Company, USA</i> and Simon G. Podkolzin , <i>Stevens Institute of Technology, USA</i> .	Session Chairs: Hongfei Lin , <i>Washington State University, USA</i> and Michael Griffin , <i>National Renewable Energy Laboratory, USA</i> .	Session Chairs: Jian Gong , <i>Cummins Inc., USA</i> and Josh A. Pihl , <i>Oak Ridge National Laboratory, USA</i> .
3:40 PM Thu-CHAB-1540 Pathways, Mechanisms, and Kinetics of Acrolein Oxidation over a Promoted Mo-V Oxide Catalyst. Jacob Miller and Aditya Bhan , <i>University of Minnesota, Twin Cities, USA</i> .	3:40 PM Thu-CHGH-1540 Hydrodechlorination of 1,2-Dichloroethane over Ag-Pd Catalysts Prepared By Controlled Surface Reactions. Madelyn Ball ¹ , Keishla Rivera-Dones ¹ , Eric Stangland ² , Manos Mavrikakis ¹ and James A. Dumesic ¹ , (1) <i>University of Wisconsin - Madison, USA</i> , (2) <i>The Dow Chemical Company, USA</i> .	3:40 PM Thu-CHIJ-1540 Nanocatalysts from Ionic Liquid Precursors for the Direct Conversion of CO ₂ to Hydrocarbons. Callum Jeffrey , Peter Nockemann and Nancy Artioli , <i>Queen's University Belfast, United Kingdom</i> .	3:40 PM Thu-CHKL-1540 In-Situ PdAu Catalytic Oxidation of Organic Compounds in Simulated Produced Water. Yiyuan Yin ^{1,2} , Kimberly Heck ² , Christian Coonrod ^{1,2} , Camilah Powell ^{1,2} , Sujin Guo ^{1,2} , Michael Reynolds ³ and Michael S. Wong ¹ , (1) <i>Rice University, USA</i> , (2) <i>Nanotechnology Enabled Water Treatment (NEWT) Center, USA</i> , (3) <i>Shell Oil Company, USA</i> .