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

Callum Jeffrey[1], Peter Nockemann[1], Nancy Artioli[1*]

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

Introduction

The direct conversion of carbon dioxide (CO_2) into gasoline range hydrocarbons (C_5-C_{11}) is a highly desirable process as a sustainable production route. 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]. Here, we propose a new ionic liquid-assisted route for the synthesis of the Iron Oxide Nanoparticles (*IONs*) resulting in improved control over size and morphology of the nanostructured material, and as a consequence, better conversion and selectivity towards the olefins.

Materials and Methods

The first method (BS-N) of the ionic liquid-assisted synthesis for the Fe_2O_3 nanoparticles involved heating of the reaction medium consisting of the ionic liquid, [C_4mim][Tf_2N] under reflux. Following decomposition, the produced Fe_3O_4 nanoparticles are separated from the reaction medium. The second method (BAC) starts the ionic liquid [bmim][OAc] and Fe(II)/Fe(III) chloride. Gentle heating (50 °C) results in precipitation of Fe_3O_4 nanoparticles. The Fe_3O_4/Zeolite catalysts were prepared by granule mixing with zeolites (HZSM(SiO_2/Al_2O_3 = 80 and 300, 1:1 ratio). The compounds were then characterised using IR, PXRD, SEM / EDX and TPR (Fig. 1). CO_2 hydrogenation reactions were performed at 320 °C, 3 MPa H /CO 3,3 in a stainless steel fixed-bed reactor with an inner diameter of 15 mm (1 g Fe_3O_4/Zeolite, reduction at 350 °C in a pure H_2 flow for 8 h). All of the products from the reactor were 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. The compounds obtained by the ionic liquid methods result in broad XRD patterns, pointing to small particle sizes (6 – 8 nm). This has also been confirmed by SEM and TEM. Characterization of the prepared catalysts by PXRD (Figure 1) shows phase purity for the magnetite obtained from both methods. Hydrogen temperature-programmed reduction (H_2-TPR) was used to determine the interaction between Fe species and the support. As shown in Figure 2 for the HZSM 300, 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 Fe_3O_4/HZSM300 prepared by both ionic liquid-assisted methods start to be reduced at slightly lower temperature compared to a reference catalyst prepared by a standard precipitation method which indicated a higher reducibility of the former catalysts resulting in higher conversion activity observed for catalysts prepared by the ionic liquid-assisted methodologies.
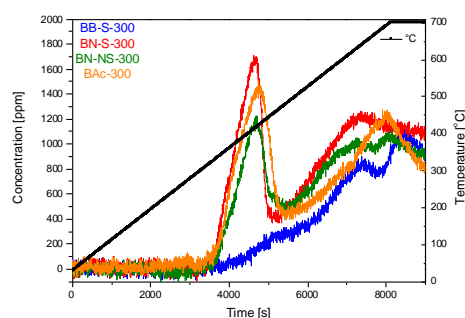

Figure 1. XRD patterns of Fe_3O_4 sample synthetised using method 1 (BN-S) and method 2 (BAC). **Figure 2.** TPR profile of 4000 ppm H_2 in Ar from r.t. to 700ºC, 5ºC/min for BN-S and BAC supported on HSM5300 and conventional Fe3O4/HSM5 300 catalyst.

Conclusions

We report here on a novel methodology for the controlled synthesis of Fe_3O_4/HZSM-5 multifunctional catalyst for the direct hydrogenation of CO_2 to gasoline. This synthesis method provides better control of size and morphology of the Fe_3O_4 nanoparticles, leading to a higher catalytic activity. The product composition can be further tuned by the choice of zeolite type, and by the choice of ionic liquid in the synthetic method. The catalytic testing under industrially relevant conditions resulted in improved selectivity to C5–C11 as well as low CH_4 and CO selectivity.

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, DOI: 10.1038/ncomms15174.