MIL-100(Fe) derived catalysts for CO$_2$ to hydrocarbons conversion

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Abstract

The conversion via reductive hydrogenation of captured anthropogenic CO$_2$ wastes into valuable hydrocarbons (e.g. fuels) with solar-H$_2$ presents an attractive concept to help reduce global warming. Notably, it would provide for the large scale conversion of energy rich solar-H$_2$ into more readily managed energy rich hydrocarbons. Coupled with CO$_2$ capture, it makes possible the potential to provide a highly reliable net zero CO$_2$ emission hydrocarbon based power generation technology. Also, it potentially provides an attractive economic case for which the cost of CO$_2$ capture can be seen as an investment, akin to that for enhanced oil recovery. This economic case would be underpinned by value addition to renewable solar-H$_2$ resources. Such CO$_2$ to hydrocarbon conversion is possible via heterogeneous catalysts. Fe, Cu, Ni, Co and Ru based catalysts, as well catalysts based on their composites, have previously shown promise for this application.

Materials with high surface area and high metal dispersion are generally preferred for heterogeneous catalysis. The broader synthetic objective seeks to transfer, and thereby capitalise on, the inherent high metal atom dispersions of metal organic frameworks (MOFs) to produce stable nanoporous materials with high metal atom / cluster dispersions and surface areas. The current study is concerned with the production, characterisation and fitness for purpose assessment of Fe-based catalysts prepared via controlled decomposition of the MOF MIL-100(Fe) to prepare products with particularly high Fe dispersions that facilitate high CO$_2$ hydrogenation activity. Silica was incorporated within the parent MOF (i) as a means for retaining the high metal atom / cluster dispersion of the parent MOF, (ii) to minimise sintering during thermal activation, and (iii) to ‘build-in’ a mechanism for catalyst regeneration (i.e. calcination) to reverse any de-activation during use by carbon deposition which can otherwise limit catalyst lifetime.

MIL-100(Fe) was decomposed via pyrolysis, both as prepared, and as thermally activated following infiltration with silica precursor (tetraethyloxydisilicate (TEOS) and 1M HCl) to provide additional silica scaffolding. Products with different Si loading were prepared via repetition of the combined infiltration and activation steps. Silica loaded pyrolysis products were additionally separately calcined to prepare a set of carbon depleted products. Physico-chemical characterisation of the products was assisted via helium pycnometry, N$_2$ sorption at 77 K, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) measurements. The potential of the products to catalyse the reductive hydrogenation of CO$_2$ into hydrocarbons was characterised via mass spectrometry ($1 - 200 \text{ m/z}$) of the gas evolved from a separate bed of each product ($40 - 80 \text{ mg}$) as supplied with 70 ml/min 1% He, 25 % CO$_2$ and 74 % H$_2$, over the temperature range 50 – 400 °C. Products were studied at pressures up to 40 bar. Additional physico-chemical characterisation of the used catalysts was conducted to investigate the effects of the catalysis conditions on the physico-chemical property evolution.
The direct pyrolysis of the MIL-100(Fe) yielded a high surface area microporous material with 49 wt% Fe content. The pyrolysis products analysed contained Fe in metallic form. The incorporation of the silica precursor led to products with framework mesoporosity not otherwise observed. The calcined products (all incorporating silica) contained Fe as Fe₂O₃. The surface area and pore volume of the initial set of silica loaded products generally decreased with their Fe content. Each of these products was found to exhibit catalytic activity which was inversely proportional to their Si loading. Catalytic activities were generally found to improve with temperature and pressure. The product prepared via the direct pyrolysis of the MIL-100(Fe) alone (no silica loading) exhibited the highest catalytic activity, consuming ~60 % of the H₂ supplied at the highest temperature and pressure tested (400 °C, 40 bar). Catalysis testing was typically found to effect a slight decrease in the products’ surface areas. Catalysis testing of the silica incorporated calcination products also led to reduction of their Fe content from Fe₂O₃ to Fe₃O₄, realising high surface area mesoporous materials with ferrimagnetic properties.

Figure 1 shows the greater H₂ consumption, and thereby catalytic activity, exhibited by the direct decomposition product (Fe-P) relative to one of the calcined (and subsequently reduced) silica loaded products (Fe-IPC) prepared via once only combined TEOS infiltration and thermal activation, as heated from 50 – 400 °C and then maintained at 400 °C for 30 min. Figure 2 shows the mass spectra 1 – 50 m/z for the same products obtained at both the beginning and end of the applied heat ramp. These results show that the consumption of H₂ corresponds with the evolution of larger m/z fragments consistent with the production of hydrocarbon species from the CO₂ and H₂ supplies. Thus these results demonstrate the promising potential of these new nanoporous Fe products to catalyse CO₂ conversion to hydrocarbons via reductive hydrogenation.

**Figure 1:** H₂ consumption by Fe-P and Fe-IPC when heated 50 – 400 °C in a stream (70 ml/min) of 1% He, 25 % CO₂ and 74 % H₂ at 40 bar.

**Figure 2:** Mass spectra (m/z 1-50) for gases evolved from Fe-P and Fe-IPC at 50 °C (blue, no conversion) and 400 °C (max. conversion), at 40 bar. Signal responses are relative to those for He tracer (m/z=4).