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The application of inelastic neutron scattering to investigate a hydrogen pre-treatment stage of an iron Fischer–Tropsch catalyst

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ABSTRACT

The effect of a hydrogen pre-treatment step on an iron based Fischer–Tropsch catalyst applied to the CO hydrogenation reaction at 623 and 723 K has been investigated by inelastic neutron scattering (INS). The catalyst cannot support methane production over a 6 h period of reaction at 623 K but it is active at 723 K. The INS spectrum indicates the presence of a predominantly aliphatic hydrocarbonaceous overlayer for the post-reaction 623 K sample, whereas the spectrum for the 723 K sample is assigned to an overlayer comprising partially hydrogenated polycyclic aromatic compounds. The hydrocarbonaceous overlayer associated with the active phase of the catalyst is modified by the hydrogen pre-treatment step. The INS spectra are interpreted with reference to microreactor studies, powder X-ray diffraction, temperature-programmed oxidation and transmission electron microscopy. The hydrogen pre-treatment stage favours the formation of amorphous carbon and is deemed not to convey any advantage with respect to CO hydrogenation activity.

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1. Introduction

Fischer–Tropsch synthesis (FTS) is making an increasing contribution to hydrocarbon production options; presently, it constitutes a vibrant area of heterogeneous catalysis research [1–3]. Recent chemical plant commissions feature unit operations utilising cobalt based catalysts [4] but there remains a significant research interest in iron based FTS catalysts, not least because these materials provide the opportunity for production of valuable unsaturated hydrocarbons [3].

This article concentrates on the surface chemistry surrounding iron based FTS catalysts and follows on from a recent realisation that inelastic neutron scattering (INS) can be used to obtain the vibrational spectrum of hydrogenous moieties present over reacted FTS catalysts [5,6]. Firstly, Hamilton and co-workers used INS to obtain the vibrational spectrum (100–4000 cm^{-1}) of an iron based

FTS catalyst taken from a large scale coal-to-liquids unit operation [5]. Secondly, a follow up communication examined an in-house iron based catalyst and used the CO hydrogenation reaction at ambient pressure to evaluate aspects of the Fe/CO/H$_2$ surface chemistry [6]. The ambient pressure measurements facilitate methane formation and discourage the chain propagation stage of the FT process, so that no high molecular weight products are formed that would otherwise complicate analysis of the INS spectra. Despite this deviation from actual FTS conditions, the INS spectrum of the model catalyst post-reaction is similar to that reported for the industrial grade catalyst and, furthermore, establishes the presence of hydrocarbonaceous overlayers when syngas is reacted over these commercially relevant materials [6].

This study similarly adopts a syngas ambient pressure regime and applies INS to examine the issue of adopting a hydrogen pre-treatment stage prior to reaction with a CO/H$_2$ mixture over the same in-house iron oxide catalyst examined previously [6]. Although industrial grade iron FTS catalysts may include promoters such as alkali metals [7–9] or other metals such as copper [9,10], this further inspection of an unpromoted iron based catalyst,

i.e. hematite, permits correlations to be made to the basic catalyst formulation, avoiding possible complications from chemical or structural promoters.

It is generally accepted that iron oxides are inactive for FTS and require pre-treatment to obtain an active catalyst [11,12]. The effect of different pre-treatments has been well reported in the literature [12–15], with the applied pre-treatment affecting the starting catalyst composition before FTS: hydrogen pre-treatment reduces the catalyst towards a mixture of magnetite and metallic iron, whilst pre-treatment in carbon monoxide or syngas leads to the formation of iron carbides; the type of carbide being dependent on the pre-treatment used [16]. Govender and co-workers [17] have shown that different pre-treatments of iron based FTS catalysts can lead to the stabilisation of different surface species under steady-state conditions. Specifically, a catalyst that experienced pre-carbidisation in carbon monoxide before FTS displayed a different reaction profile to that of a catalyst initially treated in hydrogen prior to syngas exposure. As the aforementioned INS measurements of iron based catalysts only considered catalysts exposed to syngas [6], it is opportune to investigate whether a hydrogen pre-treatment stage can perturb the form of the surface vibrational spectrum, as revealed by INS spectroscopy. Ancillary microreactor studies accompanied by powder X-ray diffraction (XRD), temperature-programmed oxidation (TPO) and transmission electron microscopy (TEM) measurements bolster the analysis of the INS spectra. Although the actual role of the hydrocarbonaceous overlayer in FTS [5] and Fe/CO/H_2 surface chemistry [6] remains uncertain, i.e. as a 'spectator' species or as an active phase [6], the heightened awareness of the presence of hydrogen incorporation in representative iron based FTS catalysts is helpful in terms of enhanced understanding of the multi-component catalyst matrix. Further, it also assists in the development of reaction mechanisms that can account for the complex product slate typically encountered in these economically relevant reactions systems.

2. Experimental

2.1. Catalyst preparation and microreactor measurements

The hematite (α-Fe_2O_3) pre-cursor catalyst used for this study was prepared by the co-precipitation technique and is described elsewhere, as is the microreactor test apparatus [6]. Briefly, the catalyst was ground and sieved to a grain size fraction of 250–500 μm. CO (99.5%, CK gas) and H_2 (99.999%, BOC) reactants were supplied at ambient pressure by mass flow controllers, using He (99.999%, BOC) as a carrier gas. Exit streams from the reactor were continuously monitored via an inline quadrupole mass spectrometer (Leda Mass, Residual Gas Analyser, LM22) that sampled the elutant gas stream via a differentially pumped capillary leak fed directly into a closed ionisation source. As noted in the Introduction section, the catalyst does not support F-T activity under these conditions; instead it favours CO hydrogenation with methane being the dominant product. Analysis of the reaction exit gas by mass spectrometry confirmed the absence of oligomeric products.

For each reaction ca. 50 mg of the precipitated α-Fe_2O_3 catalyst was used. The H_2 pre-treatment stage comprised passing diluted H_2 (30% H_2 in He at a total flow rate of 30 mL min^{-1}) prior to syngas exposure while a heating rate of 10 K min^{-1} was applied until the temperature of the sample reached 773 K, at which point the temperature was maintained for a period of 60 min. The reduced sample was allowed to cool to room temperature in flowing He then the incident gas feed was switched to a 2:1 H_2/CO mixture diluted in He (CO, 3.35 mL min^{-1}; H_2, 6.75 mL min^{-1}; He, 21.25 mL min^{-1}) at ambient pressure. These conditions provide a total weight hourly

space velocity (WHSV) [18] of 9.55 h^{-1}. A linear heating program of 5 K min^{-1} was applied up to the stated reaction temperature, where the temperature of the system was maintained for a period of 6 h. The heating program was then terminated and the catalyst sample cooled to room temperature under a flow of He. Before removal from the microreactor, passivation of reacted samples at ambient temperature was achieved using a standard procedure where the concentration of oxygen was gradually increased to 20% of the total gas feed, i.e. atmospheric levels [19]. The samples could then be analysed ex situ using XRD and TEM. It is acknowledged that these arrangements could lead to some oxidation of metallic iron, therefore detected levels of Fe^0 should be viewed as representing a lower limit. Galuszka and co-workers have shown that, provided elevated temperatures are avoided, further oxidation of carbonaceous and carbidic entities of post-reaction iron based catalyst samples operated in CO hydrogenation reactions does not occur [20].

2.2. Inelastic neutron scattering measurements

The apparatus and procedures used to prepare these in-house iron based samples for INS measurements are described elsewhere [6]. Briefly, CO (CK gas, research grade 99.97%) and H_2 (CK gas, research grade 99.999%) reactants and He (Air Products, UHP grade 99.9992%) carrier gas were supplied at ambient pressure via mass flow controllers. The reactor eluting gases were continuously sampled via a differentially pumped quadruple mass spectrometer (Spectra Microvision Plus). The reactor was charged with approximately 25 g of α-Fe_2O_3. The sample was reduced in a flow of diluted H_2 (25% H_2/He, 1 L min^{-1}) until H_2O evolution as measured by the online mass spectrometer, subsided (duration ca. 2 h) before being allowed to cool to room temperature under a constant flow of He. Reactions were then carried out using a 2:1 H_2/CO mixture diluted in He (CO, 75 mL min^{-1}; H_2, 150 mL min^{-1}; He, 775 mL min^{-1}; total WHSV = 0.54 h^{-1}) and subjected to a linear heating program of 5 K min^{-1} up to the stated reaction temperature. The reduced WHSV value for the INS reactor compared to the microreactor is acknowledged and corresponds to restrictions connected with the scale-up of the reaction for the INS measurements due to the inherent insensitivity of the INS technique. Issues connected with these constraints are explored in a previous publication [6]. Nevertheless, despite these differences, similar CH_4 yields were achievable from the microreactor and the INS reactor, indicating that comparable chemistry was being explored in both cases.

After a period of 6 h at the stated reaction temperature, the catalyst was allowed to cool to room temperature under a flow of He gas to remove residual gaseous species before being isolated and transferred to an Ar filled glove box (MBraun UniLab MB-20-G, [H_2O] < 1 ppm, [O_2] < 2 ppm). Within the inert atmosphere of the glove box, the sample was loaded into Al foil sachets, which were then secured via indium seals within a standard Al INS cell [21]. INS spectra of each of the samples were recorded at 20 K using the MAPS direct geometry neutron vibrational spectrometer located at the ISIS Facility [22]. The spectra were recorded with incident neutron energies of 4840 and 2017 cm^{-1}. Recording the INS spectrum with the MAPS spectrometer at these two incident energies facilitates the acquisition of spectra of reasonable resolution over an extended spectral range (100–4000 cm^{-1}) [22].

2.3. Catalyst characterisation

2.3.1. Pre-reaction

Before reaction testing, the precipitated α-Fe_2O_3 samples were examined using N_2 physisorption and powder X-ray diffraction (XRD). N_2 physisorption measurements were performed using a Micromeritics Gemini 2370 instrument with the surface area