Heterogeneous Catalysis

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Vibrational Analysis of an Industrial Fe-Based Fischer–Tropsch Catalyst Employing Inelastic Neutron Scattering**

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The last few decades have witnessed a resurgence of research activity into Fischer–Tropsch (F-T) catalysis, for the conversion of syngas ($CO + H_2$) into gasoline and diesel.[1] This F-T renaissance coincides with the recent commissioning of several industrial unit operations around the world.[2] Despite this range of activity, some uncertainties still remain about the actual operation of the F-T catalyst. The inherent complexity of this economically highly significant reaction system is paraphrased in Schulz's description of the active phase of a F-T catalyst as being constructed under reaction conditions during a process of self-organization.[3]

Although the new F-T unit operations tend to feature Co-based catalysts, there remains considerable interest in Fe-based catalysts. For example, Weckhuysen and co-workers have used a combination of theory and experiment to monitor in situ phase changes in Fe-based F-T catalysts.[4] More recently, studies have shown how iron-based F-T catalysts can be adapted to favor the production of low-molecular-weight olefins over high-molecular-weight alkanes.[5]

To obtain a better understanding of the function of an Fe-based F-T catalyst, we have studied an industrially reacted Fe-based F-T catalyst using inelastic neutron scattering (INS) as the principal vibrational probe because of its ability to characterize hydrogen-containing species.[6] For a description of the catalyst recovery method, see the Experimental Section. Analytical techniques such as X-ray diffraction (XRD), Mössbauer spectroscopy and temperature-programmed oxidation (TPO), are currently used to characterize iron F-T catalysts with respect to solid-state chemistry (magnetite plus iron carbides)[7] and the presence of carbonaceous materials.[8] The INS spectrometer used here (TOSCA) has been used previously to probe hydrocarbonaceous species in an industrially relevant Ni catalyst used for the dry reforming of CH_4.[9] However this work applies INS for the first time to consider the retention of hydrogenous moieties within the Fe F-T catalyst matrix. The application of INS to probe heterogeneous catalysts has been reviewed by Parker and co-workers.[10]

Elemental analysis and TPO analysis, as summarized in Table 1 and described in more detail in the Supporting Information, show that a substantial amount of carbon is retained on the catalyst together with a small but significant quantity of hydrogen. XRD analysis (see the Supporting Information) of the toluene extracted sample indicates the presence of iron carbides, which is consistent with reported findings.[8]

Table 1: Comparison of carbon and hydrogen wt% content of samples obtained using toluene and toluene/CH_2Cl_2 extraction.

Extraction	Elemental Analysis[a]		TPO[b]
	C [wt%]	H [wt%]	
toluene extraction	17.36, 17.48	0.59, 0.63	19.6
toluene/CH_2Cl_2	15.93, 15.81	0.50, 0.46	14.2

[a] Duplicate elemental analysis values for carbon and hydrogen content. [b] Carbon content as determined by temperature-programmed oxidation.

The INS spectra of the catalyst samples extracted with toluene and toluene/CH_2Cl_2 are presented in Figure 1 a,b,

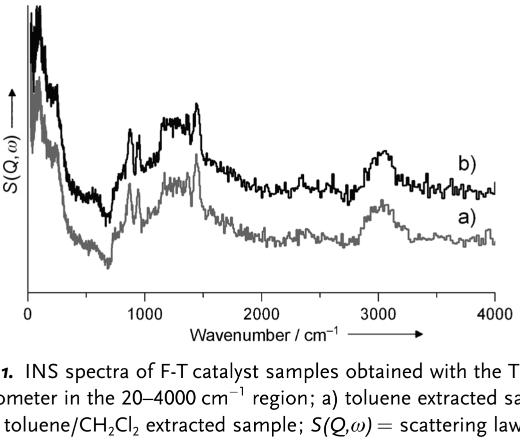

Figure 1. INS spectra of F-T catalyst samples obtained with the TOSCA spectrometer in the 20–4000 cm^{-1} region; a) toluene extracted sample and b) toluene/CH_2Cl_2 extracted sample; *S(Q,ω)* = scattering law value.

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respectively. These spectra exhibit an acceptable signal-to-noise ratio (SNR) and are virtually identical. The additional solvent power associated with CH_2Cl_2 did not consequently cause a modification of the hydrocarbonaceous overlayer retained at the catalyst surface. The degree of hydrogen retention in the catalyst sample is consistent with the proportion of retained hydrogen listed in Table 1. The spectra displayed in Figure 1 exhibit a series of distinct bands in the deformation (about 800–1450 cm^{-1}) and a relatively broad band envelope in the C–H stretch (about 3000 cm^{-1}) regions, collectively indicating the presence of hydrocarbon species, which may be discussed in terms of a hydrocarbonaceous overlayer.[11] Specifically, the band observed at about 1441 cm^{-1} in the deformation region may be assigned to the CH_2 scissoring vibration of a cycloalkane.[12] No significant intensity is apparent about 720–730 cm^{-1}, originating from in-phase rocking modes of long-chain -$(CH_2)_n$- units;[12] so the presence of long-chain aliphatic species may consequently be excluded. The band observed at about 231 cm^{-1} is attributed to a methyl torsion, which is usually located at about 250 ± 10 cm^{-1} in aliphatic hydrocarbons and exhibits considerable INS intensity.[6] Yet this torsional band is relatively weak in the measured INS spectra (Figure 1), indicating a low concentration of methyl groups. The C–H stretch region is better resolved in the INS spectrum depicted in Figure 2, clearly separating ν(C–H) stretching modes below and above about 3000 cm^{-1}, indicative of sp^3 and sp^2 hybridized carbon atoms, respectively. Curve fitting establishes approximately equal numbers of sp^3 and sp^2 hybridized C–H oscillators to be present. Nanoscale chemical imaging of an iron-based F-T catalyst by scanning transmission X-ray microscopy has previously demonstrated the formation on reaction of carbon exhibiting sp^3-like character, which was attributed to F-T reaction products.[4b] We note that there is no evidence for the presence of hydroxy groups (bands in the 3200–3600 cm^{-1} region). A vibrational assignment for Figure 1 a is presented in the Supporting Information.

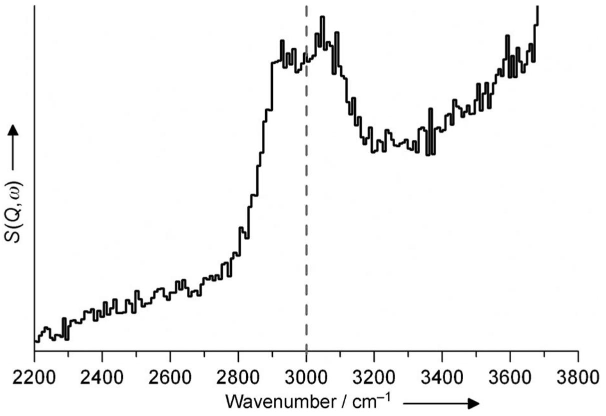

Figure 2. INS spectrum of the toluene extracted catalyst sample in the C–H stretch region[10b] obtained with the HET spectrometer.

As discussed above, the absence of any feature about 720 cm^{-1} indicates no long-chain hydrocarbons to be present. Of course, these entities would have been present on the working catalyst as products but Figure 1 shows the solvent extraction procedures have removed these materials. To justify these deductions, in the Supporting Information the catalyst INS spectrum (Figure 1 a) is compared against an INS spectrum of a combination of long chain alkanes.

Raman spectra for both catalyst samples are shown in Figure 3. Both spectra are virtually indistinguishable and dominated by the commonly observed comparatively sharp G and much broader D bands at, respectively, about 1604 cm^{-1} and 1334 cm^{-1} which are assigned to ordered and disordered sp^2 hybridized carbon atoms respectively and signify the presence of amorphous carbon. Previous Raman investigations of carbonaceous overlayers on used catalyst samples have shown the measured spectrum to be comprised of several distinct bands.[14] These are analyzed in the Supporting Information, with the spectral profiles of Figure 3 consistent with the formation of carbonaceous material.

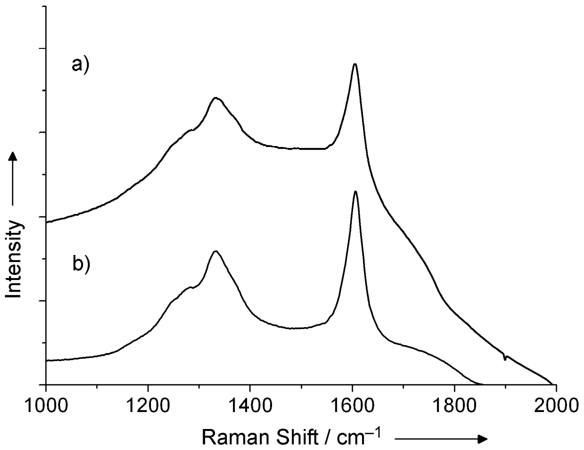

Figure 3. Raman spectra of F-T catalyst samples: a) toluene and b) toluene/CH_2Cl_2 extracted samples.

A distinct low-wavenumber shoulder is discernable at about 1255 cm^{-1} on the D band. Previous reports of Raman studies on catalytic overlayers by Castaño et al.[13] and Guichard et al.[15] assign a band recorded at about 1250 cm^{-1} to C–H deformations, whereas Ferrari and Robertson categorically state that C–H modes do not contribute to the G and D bands.[16] Although the precise origin of this shoulder is uncertain, we tentatively attribute it to a resonantly enhanced and perturbed C=C stretch within a conjugated system, which may be related to edge-decorated carbon atoms, with hydrogen being the likely partner.

The MALDI-TOF profile (see the Supporting Information) for the toluene-extracted catalyst is characterized by a complex distribution of mass fragments that increase in intensity from low mass up to about 4500 *m*/*z*, with a maximum at about 1400 *m*/*z*. The peaks are separated by about 24 *m*/*z* indicative of C_2 units and consequently signify the presence of an extended carbonaceous network. This assertion concurs with TPO measurements (Table 1).

We have used DFT calculations to simulate the INS spectra for several partially hydrogenated arenes as a model for such an amorphous carbon overlayer with a hydrocarbona-

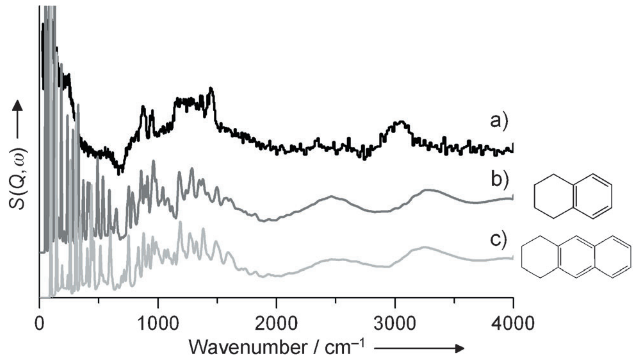

Figure 4. Comparison of the measured INS spectrum of a F-T catalyst with simulated INS spectra of partially hydrogenated arenes. a) Toluene extracted catalyst sample, b) 1,2,3,4-tetrahydronaphthalene, and c) 1,2,3,4-tetrahydroanthracene.

ceous component (for calculation description, see the Supporting Information). Figure 4 compares the measured INS spectrum of the F-T catalyst (Figure 1 a) with the INS spectra calculated for 1,2,3,4-tetrahydronaphthalene and 1,2,3,4-tetrahydroanthracene. As is evident from Figure 4, the calculations produce a series of bands in the 500–2000 cm^{-1} region, which are reminiscent of bands observed in the experimental spectrum. This is not the case at lower energy, since the measured spectrum displays a continuum with little substructure, which is commonly observed in amorphous materials and suggests that the partially hydrogenated aromatic systems do not exist as discrete molecular entities but rather as a distribution of retained hydrocarbonaceous species. Broad band envelopes in the simulated spectra positioned at about 3272 and 2474 cm^{-1} do not have any matching bands in the measured spectrum. The former band is assigned to C–H stretching modes, the energy of which is commonly overestimated in harmonic DFT calculations; no scaling factor has been applied in these simulations. The latter band represents a series of overtone and combination features arising from low-energy modes. In optical spectroscopy overtones are formally forbidden and may only appear as weak signals. However, overtones are commonly observed in neutron spectroscopy,[6] and have been accounted for in the simulated spectra. The experimental spectrum does exhibit a weak band measured at about 2360 cm^{-1}, which may be attributed to an overtone. Figure 4 may consequently be interpreted to indicate that the hydrocarbonaceous material present at the catalyst surface exhibits vibrational characteristics which are comparable to those of the model compounds.

As the nature of the retained hydrocarbon species differs significantly from the long-chain saturated hydrocarbon product typically encountered in F-T synthesis,[17] it is thought that this retained hydrocarbonaceous entity may play a role in F-T synthesis. In analogy to the concept that hydrocarbonaceous overlayers can moderate the selectivity of branching in hydrogenation reactions over supported metal catalysts,[18] we specifically suggest that the hydrocarbonaceous species characterized by the INS spectra depicted in Figure 1 may be responsible for moderating the supply of reagents within the catalyst matrix during the CO dissociative adsorption and CH_x chain propagation processes.

In summary the work here has, for the first time, used INS to obtain the vibrational spectrum of a technical-grade Fe-based F-T catalyst that has been taken from a large-scale unit operation. The vibrational spectra, elemental analysis, TPO, and the MALDI-TOF data are all consistent with the presence of an overlayer of amorphous carbon, which is supplemented to a minor extent with a hydrocarbonaceous component. INS data imply approximately equal numbers of H atoms bonded to sp^2 and sp^3 hybridized C atoms. The specific role of this previously unconsidered species in F-T process chemistry is unproven but is tentatively attributed to moderating reagent transfer at the catalyst surface. Additional INS experiments are planned to further explore the validity of this enticing hypothesis.

Experimental Section

A technical-grade iron-based F-T catalyst[19] was taken from the Secunda coal-to-liquids plant whilst the reactor was operating under steady-state conditions. The large-scale unit operation is located in South Africa and managed by Sasol Ltd.[20] On removal from the reactor the catalyst retains significant quantities of hydrocarbon product, which compromises analysis. Consequently, the solid catalyst was split into two fractions; one was Soxhlet extracted in toluene for 24 h and the other in toluene and subsequently CH_2Cl_2 for 24 h followed by a purge/drying procedure. Toluene is expected to extract all hydrocarbon products formed as part of the F-T process, whereas CH_2Cl_2 (higher polarity and dielectric constant) has the capacity to extract more complex residues. INS and Raman experiments plus DFT calculations are described in more detail in the Supporting Information.

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[1] a) E. de Smit, B. M. Weckhuysen, *Chem. Soc. Rev.* **2008**, *37*, 2758–2781; b) B. Davis, *Top. Catal.* **2005**, *32*, 3–4; c) H. Schulz, *Appl. Catal. A* **1999**, *186*, 3–12; d) M. E. Dry, J. C. Hoogendoorn, *Catal. Rev. Sci. Eng.* **1981**, *23*, 265–278; e) V. Ponec, *Catal. Rev. Sci. Eng.* **1978**, *18*, 151–171; f) M. A. Vannice, *Catal. Rev. Sci. Eng.* **1976**, *14*, 153–191.

[2] M. E. Dry, *Appl. Catal. A* **2004**, *276*, 1–3.

[3] a) M. Claeys, R. Cowan, H. Schulz, *Top. Catal.* **2003**, *26*, 139–143; b) T. Riedel, H. Schulz, G. Schaub, K. W. Jun, J. S. Hwang, K. W. Lee, *Top. Catal.* **2003**, *26*, 41–54; H. Schulz, Z. Nie, F. Ousmanov, *Catal. Today* **2002**, *71*, 351–360.

[4] a) E. de Smit, F. Cinquini, A. M. Beale, O. V. Safonova, W. van Beek, P. Sautet, B. M. Weckhuysen, *J. Am. Chem. Soc.* **2010**, *132*, 14928–14941; b) E. de Smit, I. Swart, J. F. Creemer, G. H. Hoveling, M. K. Gilles, T. Tyliszczak, P. J. Kooyman, H. W. Zandbergen, C. Morin, B. M. Weckhuysen, F. M. F. de Groot, *Nature* **2008**, *456*, 222–225.

[5] a) H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, I. Dugulan, K. P. de Jong, *Science* **2012**, *335*, 835–838; b) I. D. Gonzalez-Jimenez, K. Cats, T. Davidian, M. Ruitenbeek, F. Meirer, Y. Liu, J. Nelson, J. C. Andrews, P. Pianetta, F. M. F. de Groot, B. M. Weckhuysen, *Angew. Chem.* **2012**, *124*, 12152–12156; *Angew. Chem. Int. Ed.* **2012**, *51*, 11986–11990.

[6] P. C. H. Mitchell, S. F. Parker, A. J. Ramirez-Cuesta, J. Tomkinson, *Vibrational Spectroscopy with Neutrons*, *with Applications in Chemistry*, *Biology*, *Materials Science, and Catalysis*, World Scientific, Singapore, **2005**.

[7] a) M. D. Shroff, D. S. Kalakkad, K. E. Coulter, S. D. Kohler, M. S. Harington, N. B. Jackson, A. G. Sault, A. K. Datye, *J. Catal.* **1995**, *156*, 185 – 207; b) J. W. Niemantsverdriet, A. M. van der Kraan, *J. Catal.* **1981**, *72*, 385 – 388; c) J. W. Niemantsverdriet, A. M. van der Kraan, W. L. van Dijk, H. S. ven der Baan, *J. Phys. Chem.* **1980**, *84*, 3363 – 3370.

[8] a) T. Herranz, S. Rojas, F. J. Perez-Alonso, M. Ojeda, P. Terreros, J. L. G. Fierro, *J. Catal.* **2006**, *243*, 199 – 211; b) R. A. Dictor, A. T. Bell, *J. Catal.* **1986**, *97*, 121 – 136.

[9] I. P. Silverwood, N. G. Hamilton, J. Z. Staniforth, C. J. Laycock, S. F. Parker, R. M. Ormerod, D. Lennon, *Catal. Today* **2010**, *155*, 319 – 325.

[10] a) P. W. Albers, S. F. Parker, *Adv. Catal.* **2007**, *51*, 99 – 132; b) S. F. Parker, D. Lennon, P. W. Albers, *Appl. Spectrosc.* **2011**, *65*, 1325 – 1341.

[11] G. Webb, *Catal. Today* **1990**, *7*, 139 – 155.

[12] D. Lin-Vien, N. B. Colthup, W. G. Fately, J. G. Graselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, *1st ed.*, Academic Press, Boston, **1991**.

[13] P. Castaño, T. A. Zepeda, B. Pawelec, M. Makkee, J. L. G. Fierro, *J. Catal.* **2009**, *267*, 30 – 39.

[14] J. McGregor, Z. Huang, E. P.J. Parrott, J. A. Zeitler, K. L. Nguyen, J. M. Rawson, A. Carley, T. W. Hansen, J.-P. Tessonnier, D. S. Su, D. Teschner, E. M. Vass, A. Knop-Gericke, R. Schloegl, L. F. Gladden, *J. Catal.* **2010**, *269*, 329 – 339.

[15] B. Guichard, M. Roy-Auberger, E. Devers, B. Rebours, A. A. Quoineaud, M. Digne, *Appl. Catal. A* **2009**, *367*, 1 – 8.

[16] A. C. Ferrari, J. Robertson, *Phys. Rev. B* **2000**, *61*, 14095 – 14107.

[17] M. E. Dry, *Catal. Today* **2002**, *71*, 227 – 241.

[18] D. R. Kennedy, G. Webb, S. D. Jackson, D. Lennon, *Appl. Catal. A* **2004**, *259*, 109 – 120.

[19] Sasol Technology Limited, Advanced Synthol Catalyst.

[20] A. P. Steynberg, M. E. Dry, *Stud. Surf. Sci. Catal.* **2004**, *152*, 64 – 195.