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Mid-IR spectroscopy for rapid on-line analysis in heterogeneous catalyst testing

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Abstract

Instrumentation is reported for rapid, on-line quantitative analysis of the gaseous effluent from a heterogeneously catalyzed reaction. Absorption bands over the mid-infrared (IR) range 4000–580 cm^{-1} have been used to quantify, in less than 2 min, the major gaseous products of the hydrogenation of carbon monoxide (Fischer-Tropsch synthesis) using partial least squares (PLS) methodology. The fast analysis capability of the IR technique coupled to a single channel microreactor enables the approach of a Fischer-Tropsch catalyst to steady-state to be investigated by sampling the products every 2 min for 3 h on-stream. Coupling IR spectroscopy and chemometrics in this manner will allow a wide range of heterogeneously catalyzed reactions to be analyzed in very short times, a key requisite for high throughput catalyst testing.

Keywords: Mid-IR spectroscopy; Heterogeneous catalyst testing; Partial Least Squares methodology

1. Introduction

FT-infrared (IR) spectroscopy is routinely used in many industrial environments for process monitoring and quality control. On-line quantification of liquid and gaseous compounds is readily achieved, most commonly using near-IR (NIR) spectroscopy [1]. Mid-IR spectroscopy has been previously employed to analyze the gaseous effluent from conventional heterogeneous microreactors and it has shown great success in monitoring the exhaust gases of combustion engines and in natural gas analysis [2]. In general, the fundamental vibrations of most organic molecules lie within the spectral region 4000–600 cm^{-1} and detection of these bands can be achieved even at low concentration using IR spectrometers equipped with extremely sensitive liquid nitrogen-cooled mercury cadmium telluride (MCT) detectors. For gas analysis applications, a long path length cell is normally employed (1 m or larger) to maximize sensitivity. These long path length cells generally have large volumes (>100 cm^3), making them impractical for use in high throughput testing of heterogeneous catalysts where rapid analysis of product streams from a number of parallel microreactors is essential. For on-line FT-IR analysis to be useful in high throughput testing rapid exchange of the gas cell contents is required without contamination from the previous sample. Commercial analyzers are available with the necessary smaller volume gas cells. One example (manufactured by Temet Instruments Oy) incorporates a continuous flow cuvette of 9 cm^3 volume and 4 cm path length. This analyzer has been used to quantify gas mixtures which simulate the reaction products obtained in the dehydrogenation of *n*-butane [3]. However, even this

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cell is too large to achieve exchange of the cell contents in the timescale required for high throughput catalyst testing (generally seconds rather than minutes). Extremely low volume (ca. 0.1 cm^3) flow cells with zero dead space for FT-IR spectrometers are commercially available, but are traditionally used as IR detectors for gas chromatography, i.e. the coupled technique GC–FT-IR [4]. This technique has been applied to achieve quantitative separation and identification of components in a gas mixture [5–7], but it is most commonly used for identification of compounds as they elute from a GC column and has now been largely superseded by GC–MS technology. Generally, in GC–FT-IR it is difficult accurately to determine the concentration of a single component within the IR cell as the component is highly diluted by the carrier gas [8]. The cell or lightpipe [9] is a borosilicate capillary with an internal diameter of ca. 1 mm and a path length of several centimeters (usually 10 or greater), which has a thin gold coating on the internal surface to minimize attenuation of the IR radiation which is focused on the capillary using parabolic mirrors.

This paper describes the novel use of a GC–FT-IR detector, equipped with a 90 μl flow cell of path length 12 cm, to analyze the multi-component gas mixture produced from the heterogeneously catalyzed hydrogenation of carbon monoxide. We have studied the mechanism of this reaction for a number of years, using conventional microreactors equipped with on-line GC and GC–MS instruments [10]. These analytical techniques routinely require up to 1 h to achieve complete analysis of a sample of the reactor effluent. Clearly, to enable high throughput parallel testing of catalysts, a faster analytical technique was required to enable repetitive data collection from a number of parallel microreactors with as short a time interval as possible.

2. Experimental section

2.1. Instrumentation

In the experimental set-up (Fig. 1) the effluent from the fixed-bed microreactor (dimensions 6 mm × 200 mm) was passed through heated transfer lines (held at 140 °C) to the gas cell (path length 120 mm, radius 0.5 mm, volume 90 μl) of a Perkin Elmer Spectrum GX GC–FT-IR interface, where the pressure was carefully controlled and monitored, before flowing to a sampling valve (heated at 140 °C) attached to a Perkin Elmer AutoSystem XL/Turbomass GC–MS.

The lightpipe through which the effluent stream and IR beam pass is shown in Fig. 2. The cell is capped at both ends by KBr windows, one of which is mechanically retained and the other is held by springs to avoid over pressurization. The lightpipe could tolerate pressures of 5 psig, before leakage occurred. Throughout the calibration of the IR analyzer and catalyst testing the lightpipe was held at a constant pressure of 4 psig. The total pressure in the lightpipe was tightly controlled to maintain a constant concentration of gases in the lightpipe and provide consistency between one effluent stream and another. This was achieved by installing a pressure control loop comprising an MKS 148J solenoid valve upstream of the lightpipe that constantly adjusted to the pressure registered by an MKS

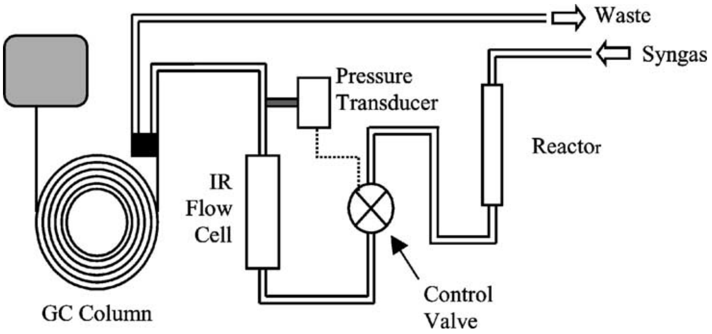

Fig. 1. Schematic representation of the experimental apparatus—flow path and hardware components.

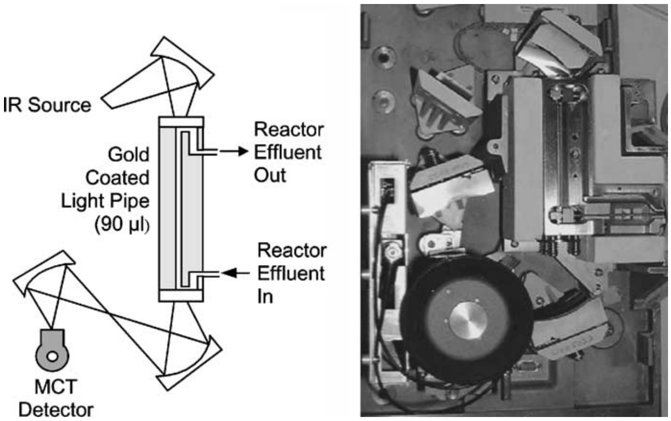

Fig. 2. Schematic diagram and photograph of IR light path in GC–IR interface.

Baratron 221B differential pressure transducer downstream of the lightpipe. This allowed the pressure to be controlled and maintained in and across the lightpipe at 4 ± 0.02 psig. The solenoid valve and pressure transducer were heated to 150 °C to avoid condensation. In addition, to monitor the pressure of gases entering the microreactor, a second pressure transducer was positioned downstream of the reagent gas mixing chamber. The minimization of dead space was desirable throughout the instrumentation and essential within the lightpipe to allow high flushing rates so that many different samples could be analyzed sequentially. Fig. 3 shows that using a flow rate of 0.6 l/h, carbon monoxide flowing through the lightpipe could be exchanged for hydrogen in less than 6 s.

2.2. Calibration of GC–MS

GC–MS was an integral part of analysis as it enabled the calibration of the IR spectra, by recording a library of standard spectra of known composition to build a model for the quantification software [11].

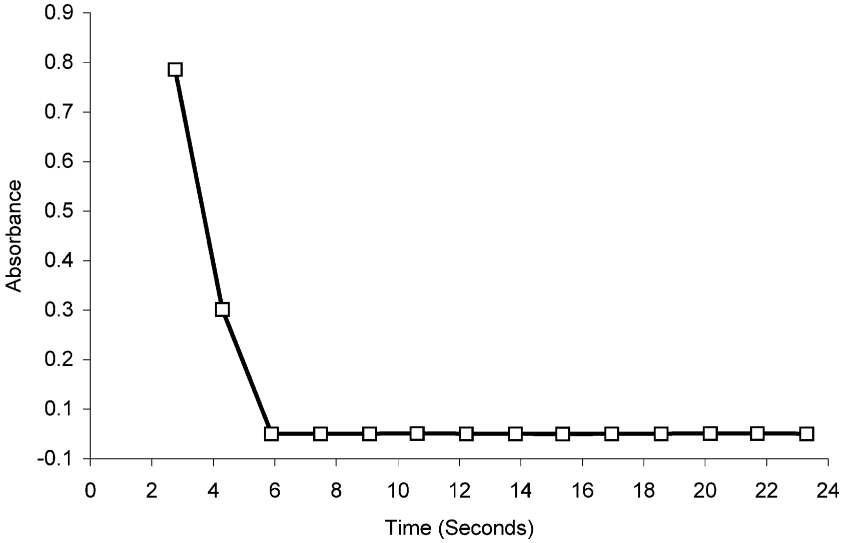

Fig. 3. Exchange of carbon monoxide for hydrogen—plot showing intensity of CO stretch (2183 cm^{-1}) after gas switched from $CO:2H_2$ to pure H_2 (8 cm^3/min).

It was also used to provide quantification of effluent product streams to check the validity of the IR results and to provide a more complete quantification, beyond C_4 components, when needed. The GC–MS was fitted with a 0.125 cm^3 automatic injection sample loop and was used with a 1:20 split onto a Perkin Elmer (60 m × 0.32 mm × 5 μm) column in order to achieve similar sensitivity to the IR analyzer. A sub-ambient cooling facility allowed the GC oven to be cooled to 0 °C which was needed to resolve the carbon monoxide and methane peaks satisfactorily. A temperature program lasting 16 min was developed to resolve all the components necessary in calibrating the IR analyzer. In order to calibrate the GC–MS a custom made mixture of carbon monoxide containing 3.1% cyclopropane (BOC) was used as an internal standard. Firstly, the components of syngas (hydrogen and CO, containing the cyclopropane) were mixed and then known amounts of the analyte were added and the resulting mixture flowed through the FT-IR analyzer and finally injected into the GC–MS. The concentration of the analyte was adjusted by careful pressure regulation.

2.3. Calibration of the FT-IR analyzer and collection of IR spectra

Calibration of the IR spectrometer was achieved by flowing gas mixtures through the lightpipe, while recording their IR spectra and then quantifying the components of the same gas mixtures by GC–MS. In order for the chemometrics software to be able to quantify unknown gas mixtures, IR spectra were collected of all the expected components at their expected concentrations. The gas mixtures were produced by injecting various amounts of pure compounds into a glass tube filled with synthesis gas and then flowing metered syngas through the tube to produce a gas flow to the lightpipe and the GC–MS. The concentrations of the components bracketed those expected for the gaseous effluent of the catalysis and the composition data of the gas mixtures were then input into the chemometrics program [11], to generate a library of standard IR spectra. A scan range of 4000–580 cm^{-1} and a spectral resolution of 1 cm^{-1} were used for the IR data collection. Spectra of gas mixtures were collected in preference to those of pure components, to take into account any possible interactions between the components and to model overlapping absorption bands accurately. The two analysis techniques differed in their sampling, with the GC–MS utilizing batch flow and the IR dynamic flow procedures, respectively. To ensure that the data collection was comparable, the injection of the sample onto the GC column was timed to correspond with the middle of the IR data collection. This allowed for any small change in component concentration during the time taken to collect the IR spectrum. Numerous (86) gas mixtures were prepared and analyzed to give a robust model for the analysis.

2.4. Chemometrics calibration methods

Three analysis methods using a partial least squares (PLS) algorithm were developed within the chemometrics program [11] utilizing different areas of the mid-IR region, to quantify, respectively:

- Alkanes from methane to butane, using the spectral regions 3245–3022 and 3007–2612 cm^{-1}.
- Alkenes from ethene to butene and the oxygenates, methanol and ethanol, using the spectral region 1148–896 cm^{-1}.
- Carbon monoxide, carbon dioxide and water using the spectral regions 4000–3775, 2470–2200, 2080–1604 and 712–640 cm^{-1}.

These regions were carefully selected to correspond to the strong and distinctive absorption bands of each component. Areas of very strong absorption bands (above 0.7 units) and noise were omitted, or blanked, from the calibration calculations. An indication of the quality of fit was given by the residual spectrum (the difference between the measured and calculated spectra). A high quality fit resulted in the residual spectrum containing only noise, while any structure in the residual spectrum indicated that the unknown sample had features not modeled, or that the absorption bands were more intense than those in the calibration set.

2.5. Hydrogenation of carbon monoxide

Heterogeneous catalysts were prepared by standard impregnation of the support (Davisil grade 646 silica gel) with aqueous solutions of the metal salts to incipient wetness. The preparation, reduction and activation of the catalysts have been described in detail previously [12]. A catalyst (1 g) was loaded into a fixed-bed microreactor (6 mm × 200 mm) and reduced under flowing hydrogen (1.8 l/h) by programmed heating from room temperature to 400 °C at 4 °C/min. The catalyst was cooled to the desired reaction temperature under hydrogen and a background spectrum recorded with the lightpipe filled with hydrogen. Synthesis gas (H_2:CO typically in a 2:1 ratio) was then supplied to the microreactor held at the desired reaction temperature using a flow rate of between 0.6 and 1.8 l/h, maintained using MKS Instruments calibrated mass flow controllers. The effluent flow passed through the lightpipe, set at 200 °C and 4 psig. IR spectra of reactor effluent were recorded at intervals, either during or after the attainment of a steady-state condition, and quantified using the chemometrics procedure described above.

Table 1
Comparison of simultaneous analyses of 6% Rh/2% Co catalyst at 230 °C after 2 h on-stream

Product	GC–MS (ppm)	FT-IR (ppm)
CO	277968 ± 4200	282470 ± 4200
CO_2	2048 ± 30	2128 ± 30
H_2O	93054 ± 1400	87677 ± 1400
CH_4	77065 ± 4200	78203 ± 4200
C_2H_4	Unobserved	55 ± 1
C_2H_6	9253 ± 140	8711 ± 140
C_3H_6	553 ± 10	642 ± 10
C_3H_8	17074 ± 250	15314 ± 230
C_4H_8	936 ± 20	1165 ± 20
C_4H_{10}	7509 ± 110	8697 ± 130
MeOH	10731 ± 160	9768 ± 150
EtOH	41281 ± 620	39152 ± 590

3. Results and discussion

The heart of the new instrumentation for the rapid on-line quantitative analysis of the gaseous effluent from a catalytic microreactor equipment is a conventional GC–FT-IR detector and the complete system is shown in Figs. 1 and 2. Detailed installation/calibration procedures are set out in the experimental section. Initial experiments were carried out to determine the number of scans required to achieve adequate signal to noise for a robust quantification using the FT-IR spectrometer. Fifty scans at $1\,cm^{-1}$ resolution gave acceptable results with little improvement evident on increasing the number of scans. Whilst lower spectral resolution offers some advantages [13], for example, where the use of sensitive liquid nitrogen-cooled detectors is impracticable and the spectral analysis speed and dynamic range need to be fully optimized, the increased sensitivity achievable with higher spectral resolution was important in the present research, particularly when working at low product conversions.

The apparatus described above was employed to quantify the products of the hydrogenation of carbon monoxide over a supported transition metal catalyst. The products of the reaction are predominately straight-chain hydrocarbons and water, with some oxygenates and carbon dioxide. It was desirable to detect all the major IR-active components in the effluent stream, namely all isomers of C_1–C_4 hydrocarbons, carbon monoxide, carbon dioxide, water, methanol and ethanol to provide a complete carbon mass balance for the reaction. This was achieved by building a robust calibration model with a spectral library of 86 separate mixtures for quantification using the PLS methods as implemented in the commercial chemometrics software [11]. The catalysts employed were based on rhodium and cobalt, supported on silica. These metals, which preferentially produce relatively short-chained hydrocarbons and oxygenates under selected operating conditions were preferred for two reasons: (i) beyond C_4, the IR spectra of the individual hydrocarbons become too similar to distinguish; and (ii) high molecular mass hydrocarbons can cause blockage in the narrow bore transfer lines. For this reason ruthenium-based catalysts were avoided [14].

To test the success of the calibration and the accuracy of the quantification, the reaction of CO/H_2 (1:2) over a 6% Rh/2% Co/silica catalyst at 230 °C was conducted, and the data obtained by simultaneous FT-IR and GC–MS analyses are collected in Table 1.

The largest differences in results between the two techniques were initially observed for CO_2 and H_2O. This was due to fluctuations in concentrations of these components within the ambient atmosphere of the GC–IR interface through which the IR radiation passes en route to and from the lightpipe. To counter this, the atmosphere was stabilized by flushing the interface with high purity nitrogen, provided by a nitrogen generator, at a rate of 6 l/min. The generator operated continuously so that the need for running

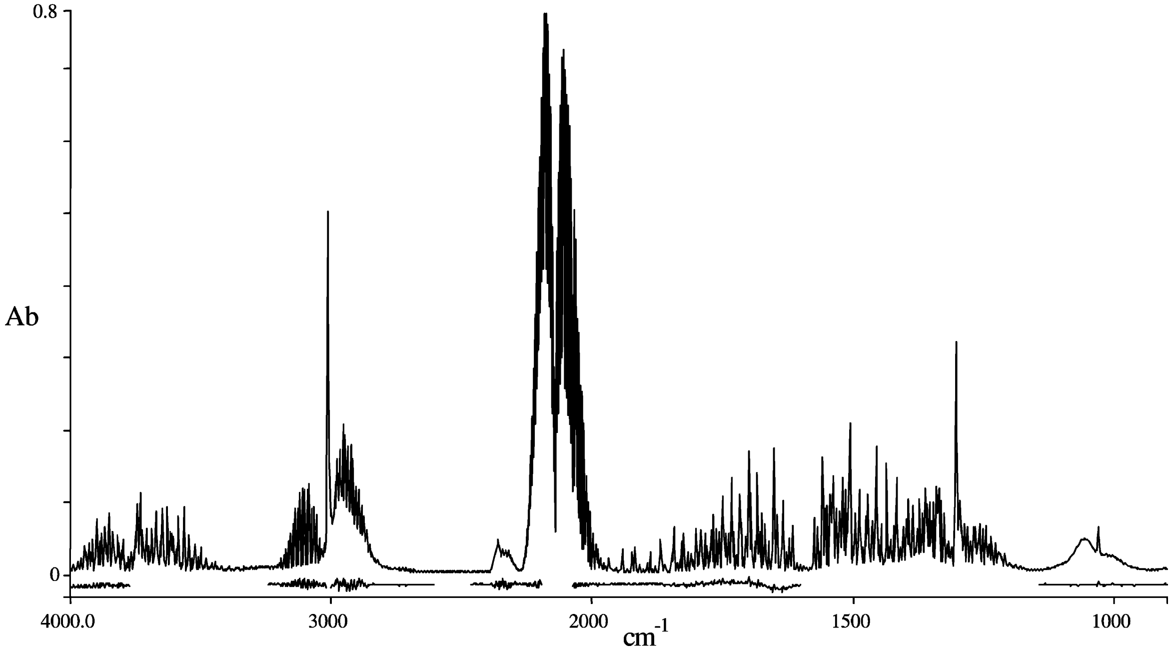

Fig. 4. IR Spectrum of effluent from a 6% Rh/2% Co catalyst at 230 °C after 2 h on-stream and subtracted fits.

background spectra periodically throughout the day was reduced. This was particularly advantageous when conducting a substantial number of microreactor tests as the instrumentation could be used on demand, allowing longer testing times. Discrepancies between the GC–MS and IR analyses were also found for ethane and propane, with the IR analysis slightly over-emphasizing the ethane contribution and slightly under-emphasizing the propane. This was because of the very similar absorption bands of these compounds in the ν(C–H) region of the spectrum and the lack of any other suitable absorption bands to distinguish the two components. Hakuli et al. [3] have also reported this problem with the quantification of ethane and propane. It is clear from Table 1 that the two techniques give comparable results with the fundamental difference being the time taken to obtain the data. The turnaround time for consecutive measurements was 30 min for GC–MS but less than 2 min for the FT-IR method. An IR spectrum of the catalyst effluent, taken after 2 h on-stream acquired using 50 scans at 1 cm^{-1} resolution to obtain a satisfactory signal to noise ratio, is shown in Fig. 4, together with the residual spectrum resulting from subtraction of the calculated spectrum. The presence of only noise in the residual spectrum clearly indicates the high quality of the calibration model.

Having established the fast analysis capability of the on-line FT-IR technique, its potential was investigated by studying, in real time, the approach of the catalyst activity to steady-state after being brought on-stream [15]. To compare catalyst performance, it is essential that catalysts should be tested under steady-state conditions to ensure comparable and reproducible results between catalysts. Traditional GC methods are not fast enough to allow real time monitoring of all components during the approach to steady-state in this reaction. Using the FT-IR method, catalyst activity was monitored every 2 min after being brought on-stream. For this experiment, the same catalyst composition employed, 6% Rh, 2% Co (w/w) supported on silica, but held at 215 °C under a flow of synthesis gas (CO: $H_2 = 1:2$, 1.8 l/h). These results are shown in Fig. 5.

The plot shows that the catalyst approaches a steady-state condition after about 1 h on-stream with slow deactivation being evident after this time. The potential problem of not analyzing at steady-state is apparent from the trace for methane, which shows

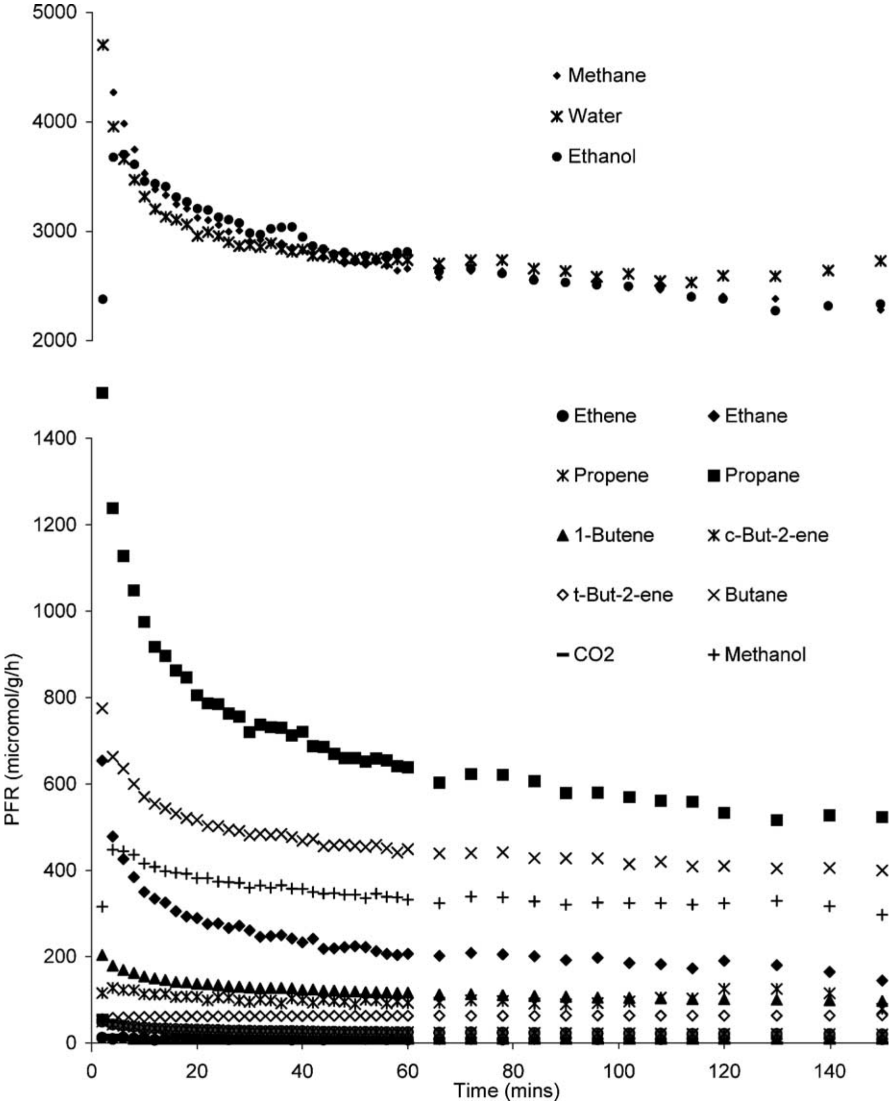

Fig. 5. Plot of product formation rate (*y* axis nmol) against time on-stream (*x* axis min) from a 6% Rh/2% Co catalyst held at 215 °C.

an initial high rate of formation but then falls significantly over the first 30 min of reaction. However, after that, the rate stabilized for the remaining time of reaction.

To compare catalyst performance, it is of vital importance to know the errors inherent in the data so that the level of discrimination that is significant between two data points can be judged. The total errors inherent in the analysis were examined by analyzing five separate spectra taken consecutively over a 15-min period, after syngas (0.9 l/h) had been passed over a 5% Co/1% Cu/0.2% Li/silica catalyst at steady-state at 230 °C. Errors in the analysis arose from the variation in (i) the total gas flow and its composition; (ii) the temperature of the catalyst and the lightpipe; (iii) the pressure within the lightpipe; (iv) the intensity of IR radiation received by the IR detector and (v) the extent to which the catalyst was truly at steady-state. Fig. 6 shows the variation in the five FT-IR spectra of the products in the ν(C–H) region when overlaid,

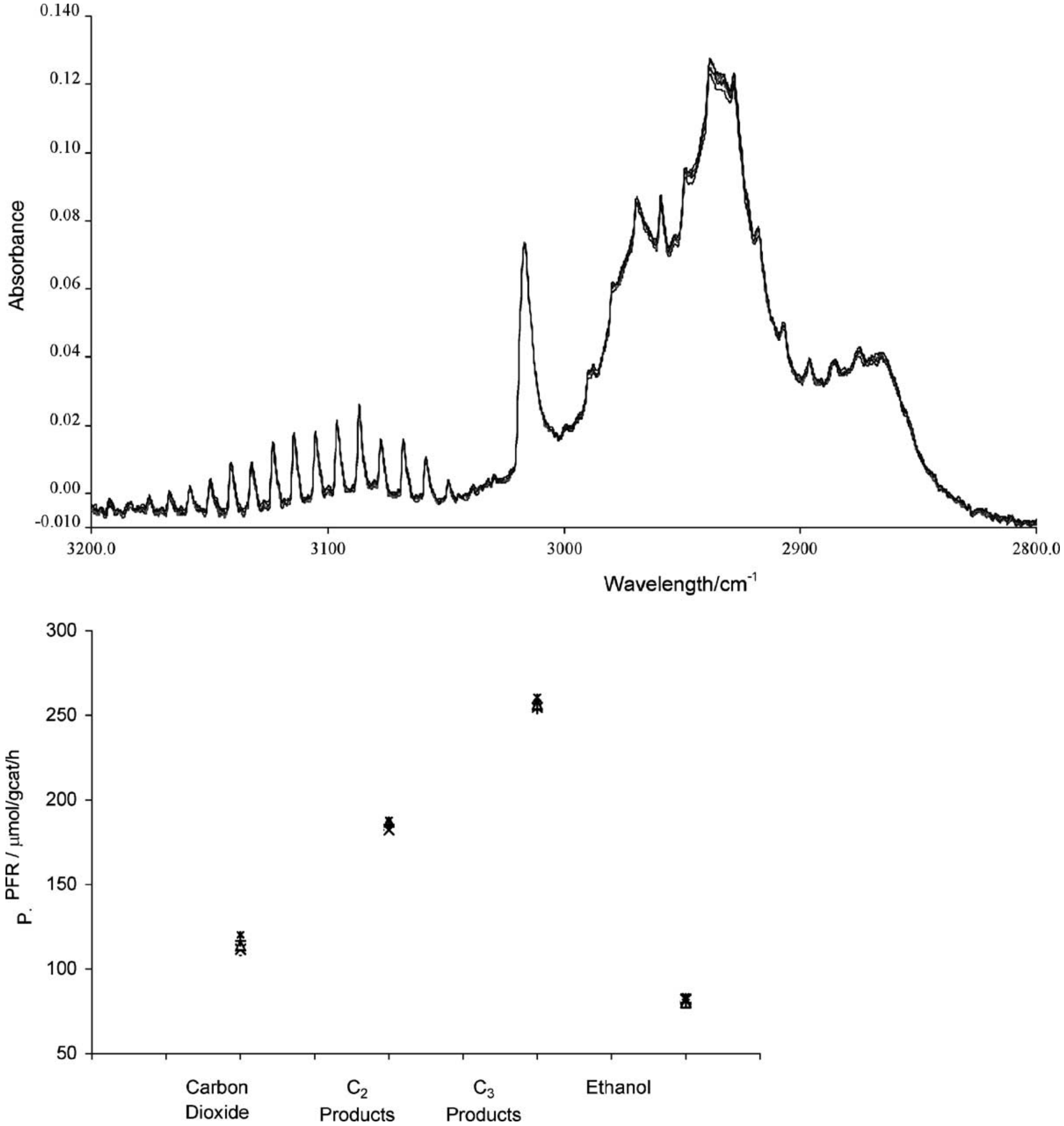

Fig. 6. Visual variation in FT-IR spectra collection in ν(C–H) region over 15 min and variation in IR analysis for selected components for a 5% Co/1% Cu/0.2% Li/silica catalyst at steady-state at 230 °C.

with the resulting variation in quantitative analysis for selected components.

The measured product concentrations of each component in Fig. 6 vary by up to 2% from the mean, except CO_2 which as mentioned previously shows larger errors and may vary up to 5% from the mean value. These values represent the total errors associated with the experiment and are comparable, if not better, than the errors inherent in on-line analysis using conventional GC with FID or MS detectors.

4. Conclusions

Mid-IR spectroscopy has been employed for rapid, on-line analysis of the gaseous effluent from a heterogeneous catalytic reaction in a conventional microreactor. The critical part of the instrumentation employed is an extremely low volume (90 μl) gas cell or lightpipe such as is normally used in FT-IR detectors for GC. The utility of the new instrument has been demonstrated by quantitative analysis of complex product gas mixtures from the hydrogenation of carbon monoxide over heterogeneous Co/Rh/silica catalysts. The contents of the lightpipe can be exchanged in a few seconds, and the pressure within the cell can be maintained to an accuracy of ±0.02 psig at 4 psig. In order to gain high spectral definition, 1 cm^{-1} resolution was used in the data collection and signal averaging of 50 scans was required to produce a satisfactory signal to noise ratio. Under these operating conditions, the quantification of the gaseous effluent was possible in 2 min, in contrast to 30 min by conventional GC techniques. This enhanced speed of analysis has allowed a study of the approach of the catalyst to a steady-state condition to be monitored in real time. The estimated errors for the analysis using FT-IR spectroscopy are comparable or better than those achieved using conventional GC–FID or GC–MS techniques. Extension of this work to the use of on-line FT-IR analysis for high throughput parallel testing of heterogeneous catalysts is under development.

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References

[1] J.J. Workman, Appl. Spectrosc. Rev. 34 (1999) 1.
[2] D. Qin, G. Cadet, Anal. Chem. 69 (1997) 1942.
[3] A. Hakuli, A. Kytökivi, E.-L. Lakomaa, O. Krause, Anal. Chem. 67 (1995) 1881.
[4] P.G. Griffiths, J.A.D. Haseth, L.V. Azzeraga, Anal. Chem. 55 (1983) 1361A.
[5] D.T. Sparks, R.B. Lam, T.L. Isenhour, Anal. Chem. 54 (1982) 1922.
[6] D.F. Gurka, I. Farnham, B.B. Potter, S. Pyle, Anal. Chem. 61 (1989) 1584.
[7] J.W. Diehl, J.W. Finkbeiner, F.P. DiSanzo, Anal. Chem. 65 (1993) 2493.
[8] N. Ragunathan, K.A. Krock, C. Klawun, T.A. Sasaki, C.L. Wilkins, J. Chromatogr. A 856 (1999) 349.
[9] L.V. Azzeraga, Appl. Spectrosc. 34 (1980) 224.
[10] R. Quyoum, V. Berdini, M.L. Turner, H.C. Long, P.M. Maitlis, J. Catal. 173 (1998) 355;
I.M. Saez, N.J. Meanwell, A. Nutton, K. Isobe, A. Vázquez de Miquel, D.W. Bruce, S. Okeya, D.G. Andrews, P.R. Ashton, I.R. Johnstone, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1986) 1565.
[11] Perkin-Elmer Quant^{+} Software.
[12] M.L. Turner, H.C. Long, A. Shenton, P.K. Byers, P.M. Maitlis, Chem. Eur. J. 1 (1995) 549.
[13] P. Jaakkola, J.D. Tate, M. Paakkunainen, J. Kauppinen, P. Saarinen, Appl. Spectrosc. 51 (1997) 1159.
[14] M.A. Vannice, J. Catal. 37 (1975) 449.
[15] A. Hakuli, A. Kytökivi, O.I. Krause, T. Suntola, J. Catal. 161 (1996) 393.