



ELSEVIER

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Neutron spectroscopy studies of methanol to hydrocarbons catalysis over ZSM-5

A. Zachariou^{a,c}, A. Hawkins^{a,c}, S.F. Parker^b, D. Lennon^c, R.F. Howe^{d,*}

^a UK Catalysis Hub, Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Chilton, Oxon OX11 0FA, UK

^b ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Oxon OX11 0QX, UK

^c School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK

^d Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, UK

ARTICLE INFO

Keywords:

Inelastic neutron scattering

Zeolite ZSM-5

Methanol to hydrocarbons

ABSTRACT

This article reviews recently published work showing how inelastic neutron scattering spectroscopy can be used to identify species found in zeolite ZSM-5 used as a catalyst for conversion of methanol to hydrocarbons. The advantages and disadvantages of the technique are illustrated, and current challenges identified.

1. Introduction

Infrared spectroscopy has been a powerful technique in catalysis research for more than 60 years, being used for characterisation of catalyst materials, observation of active sites and adsorbed species and, more recently, in *operando* studies of catalyst surfaces under reaction conditions [1]. The complementary vibrational technique of Raman spectroscopy has been less widely used, being in many cases being restricted by low sensitivity and sample fluorescence [2]. Both infrared and Raman spectroscopy are, of course, based on quantum mechanical selection rules; a vibration must involve a change in dipole moment for an infrared absorption band to be observed, while a change in polarizability is required for a vibrational mode to be Raman active. The relative intensities of different modes may differ by several orders of magnitude (and in the case of Raman spectroscopy be dramatically enhanced by resonance effects). Observation of infrared spectra of adsorbed species on a catalyst surface may be greatly hindered by the presence of strong absorption bands from the underlying catalyst.

Inelastic neutron scattering spectroscopy (INS) offers several advantages over infrared and Raman spectroscopy for the observation of vibrational spectra of adsorbed molecules, as discussed further below. This review focusses on the use of INS to investigate zeolite catalysts for the conversion of methanol to hydrocarbons. The high internal surface area of zeolites offers sensitivity advantages for all spectroscopic techniques. The potential of INS for studying zeolite catalysts was recognised in early studies of the OH bending modes of the acidic hydroxyl groups in zeolite Rho [3] and HY [4], and Jobic [5] first showed that the lower frequency vibrational modes of benzene adsorbed in NaY

could be seen by INS without interference from zeolite modes. The recent work reviewed here emphasises the particular value of INS for probing a working catalyst.

2. Inelastic neutron scattering

INS is formally analogous to Raman spectroscopy in that it is an inelastic scattering process and the difference in energy between the incident and the scattered beams correspond to vibrational modes of the sample. However, the underlying physics is quite different: for Raman spectroscopy the probe is a photon scattering while for INS it is a neutron. The key difference is that neutrons have mass (1.008 amu) and consequently any scattering event results in a change of the neutron's momentum (Q , \AA^{-1}). Neutrons are scattered by the nuclei of the sample atoms and the observed intensity, $S(Q, \omega)$, is given by [6]:

$$S(Q, n\omega_i) \propto \frac{(QU_i)^{2n}}{n!} \exp(-(QU_{Tot})^2) \sigma \quad (1)$$

where ω_i is the i th mode at frequency ω , $n = 1$ for a fundamental, 2 for a first overtone or binary combination, 3 for a second overtone or ternary combination *etc.*, Q is the momentum transfer, U_i is the root mean square displacement of the atoms in the mode and σ is the inelastic scattering cross section of the atom. The exponential term in Eq. (1) is a Debye-Waller factor, U_{Tot} is the total root mean square displacement of all the atoms in all the modes, (both internal and external), and its magnitude is in part determined by the thermal motion of the molecule. This can be reduced by cooling the sample and so spectra are typically recorded below 30 K.

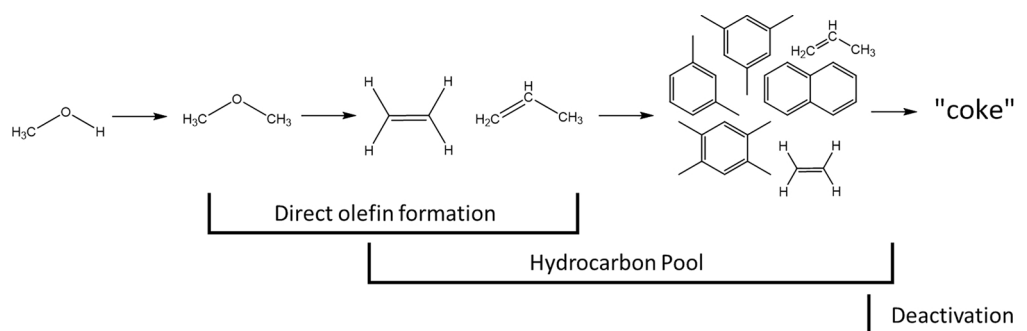
* Corresponding author.

E-mail address: r.howe@abdn.ac.uk (R.F. Howe).

<https://doi.org/10.1016/j.cattod.2020.05.030>

Received 31 January 2020; Received in revised form 19 April 2020; Accepted 6 May 2020

0920-5861/© 2020 Elsevier B.V. All rights reserved.



Scheme 1. Reaction sequence in MTH chemistry.

Eq. (1) shows that the intensity is proportional to the product of the momentum transfer squared, the incoherent scattering cross-section of the target nucleus, the amplitude of the vibration and is damped by the Debye Waller factor. Note that Eq. (1) is purely mechanical: there are no electronic factors which means that there are no quantum mechanical (symmetry based) selection rules and, in principle, all vibrations are observable. However, the incoherent scattering cross-section of the hydrogen nucleus is more than 10 times larger than that of any other nucleus, which means that INS will most readily detect vibrations involving hydrogen atoms.

There are two classes of INS spectrometer: indirect and direct geometry. The two types are complementary and for the present purposes the key difference is that indirect geometry spectrometers provide good resolution spectra up to 2000 cm^{-1} , while direct geometry spectrometers cover the entire $0\text{--}4000\text{ cm}^{-1}$, albeit with modest resolution, but crucially provide access to the C–H and O–H stretch region. For a fuller description of the physics of INS, the generation of neutron beams and the merits of direct *versus* indirect spectrometers, the reader is referred to review articles and book chapters [6–11].

For measurements on catalyst samples, an important additional issue is the presentation of sample to the neutron beam. Unlike infrared spectroscopy, no particular sample preparation is required for INS; measurements can be made on fine or coarse powders, commercial catalyst pellets or even monoliths. The sample must be contained within a sample cell, which may be aluminium, nickel stainless steel, quartz, etc. and mounted in a cryostat at 20 K or less to minimise the Debye-Waller factor's damping of the intensity, see Eq. (1). For this reason *operando* measurements under reaction conditions remain challenging. If the sample cell is used as a reactor, this must be closed, taken off-line and transferred to the INS cryostat for measurements. Alternatively, catalyst samples can be taken from a reactor and loaded into INS sample cells in a glove box. Examples of sample cell geometries are given in reference [12].

Applications of INS to catalysis reviewed elsewhere include observation of hydrogen adsorbed on supported metal catalysts, hydrocarbon species on Fischer-Tropsch catalysts, alcohols and other reactants adsorbed on activated carbon or oxide catalyst surfaces. The advantages of INS over infrared spectroscopy for these systems (ability to see all vibrational modes of hydrogen containing species without obscuration by catalyst modes, independence of sample morphology and geometry) have been clearly shown [6,10,11]. We should not omit the limitations of the technique. It is relatively insensitive: typically 5 g or more of catalyst is required and measurement times can be up to 8 h or more. Neutron sources with the flux needed for INS are scarce: Parker and Collier [9] recently identified four facilities world-wide currently operating broadband ($0\text{--}4000\text{ cm}^{-1}$) INS spectrometers (ISIS in the UK, ILL in France, SNS in the US and JPARC in Japan), although new facilities are also under construction in China and Sweden and there are several facilities that can measure spectra up to 800 cm^{-1} or so. The energy resolution can never match that of infrared or Raman spectroscopy, and true *operando* measurements are improbable at this

time. Nevertheless, as discussed here, INS can provide important new information about adsorbed species in catalysts not accessible by other techniques.

We review here INS measurements undertaken at the ISIS neutron source using two direct geometry spectrometers (MERLIN and MAPS) and an indirect geometry instrument (TOSCA) on zeolite catalysts used for the conversion of methanol to hydrocarbons (MTH).

3. Methanol to hydrocarbons

The MTH process first developed in the 1980s provides a route from natural gas to olefins for polymer production or to gasoline as a transport fuel [13]. The aluminosilicate zeolite ZSM-5 is the preferred catalyst for gasoline formation from methanol (MTG), while a smaller pore less acidic silico-aluminophosphate zeolite SAPO-34 is used to convert methanol selectively to light olefins (MTO). The MTO process has recently become prominent in China for production of olefins from coal [14].

MTH chemistry is complex. Scheme 1 illustrates the overall reaction sequence without providing any mechanistic insight.

Three stages in the reaction profile have been identified: (i) the initial formation of carbon-carbon bonds from methanol and dimethyl-ether through a so-called direct mechanism, (ii) the steady state production of olefins and/or aromatic gasoline components through an indirect mechanism involving a pool of olefinic and aromatic hydrocarbon species (the “hydrocarbon pool”) within the zeolite pores, and (iii) the final stage of catalyst deactivation through coke formation and blockage of the zeolite pores. Understanding the reaction pathways involved in both the direct and indirect processes is important in optimising the catalyst activity and selectivity to desired products, while understanding and controlling catalyst deactivation is crucial to operation of commercial MTH plants. Recent reviews summarise current understanding of MTH chemistry [15,16].

A number of different spectroscopic techniques have been applied to try and identify hydrocarbon species present in MTH catalysts under reaction conditions. NMR spectroscopy has observed a range of cyclic alkenyl and aromatic species formed when methanol is reacted over ZSM-5 or SAPO-34 at temperatures above 250 C [17]. These species are also seen by UV-vis spectroscopy [18]. Infrared spectroscopy is particularly powerful for observing the initial stages of the reaction when methanol first encounters the acid sites in the zeolite catalyst [19–21]. The infrared method suffers however from some limitations. The spectral range available to observe adsorbed hydrocarbons is limited by intense absorption bands between 1100 and 1400 cm^{-1} and below 900 cm^{-1} due to stretching and bending modes of the aluminosilicate or aluminophosphate framework. The intense electronic absorption bands of cycloalkenyl and aromatic cation species found in the hydrocarbon pool (observed by UV-vis spectroscopy) extend into the infrared region of the spectrum and cause an increase in baseline absorbance which can obscure infrared active vibrational modes of these and other species. This is particularly problematic in deactivated catalysts, which

are black in colour and give poor quality infrared spectra.

3.1. Methanol in HZSM-5 at low temperature

The first steps in reaction of methanol in a zeolite catalyst are adsorption and dissociation of the methanol at the Bronsted acid sites in the zeolite. The reaction sequence can be represented as:



i.e. initial hydrogen bonding of methanol to the zeolite OH group followed by dissociation of the methanol to form surface methoxy groups and water.

Infrared spectroscopy provides clear evidence for surface methoxy group formation at temperatures of 200 C or above [20]. At lower temperatures, the infrared spectrum of methanol in ZSM-5 is dominated by bands assigned to hydrogen bonded species, although recent infrared evidence has been presented for some surface methoxy group formation even at room temperature [22]. Infrared spectroscopy cannot however quantify the extent of methanol dissociation, since the intensities of infrared bands depend on extinction coefficients which can vary over many orders of magnitude. In particular, hydrogen bonding is known to greatly enhance the extinction coefficients of $\nu(\text{OH})$ modes in zeolites [23], although the effects of hydrogen bonding on extinction coefficients of associated $\nu(\text{CH})$ modes in for example adsorbed methanol, is not well understood.

INS intensities for vibrational modes involving hydrogen atoms are independent of extinction coefficients. O'Malley et al. [24] have reported INS spectra of methanol adsorbed at room temperature in ZSM-5 and a dealuminated HY zeolite (chosen to have a similar acid site density as the ZSM-5). Fig. 1 shows the spectra measured on the direct geometry MAPS instrument at two different incident neutron energies.

The INS spectra of both blank zeolites (measured after removal of adsorbed water) show weak bands at $\sim 3600 \text{ cm}^{-1}$ due to OH stretching modes of the Si(OH)Al groups in the zeolite which are the

Bronsted acid sites and a corresponding bending mode at $\sim 1100 \text{ cm}^{-1}$. Note that the spectroscopic resolution in the lower frequency region is much enhanced when a lower incident energy neutron beam is used; this is a feature of INS spectra measured with a direct geometry spectrometer. The OH stretching and bending modes are both extremely weak in the INS because of the low concentration of acid sites in the HZSM-5 and dealuminated HY zeolites. Adsorption of methanol into zeolite HY (Fig. 1 (a) and (b)) gives INS spectra closely similar to those of solid methanol, with one obvious exception. The band at around 3000 cm^{-1} is due to CH stretching modes of the methanol, with a higher frequency shoulder due to the methanol OH stretching mode. Both features still appear to be present in the spectrum of adsorbed methanol. Bands at 1490 and 1160 cm^{-1} in the spectrum of methanol are due to CH_3 bending and deformation modes respectively and these are unchanged in the spectrum of the adsorbed methanol. The band at around 750 cm^{-1} in Fig. 1(a) which appears as a well resolved doublet in the lower energy excited spectrum in Fig. 1(b) is assigned to OH deformation modes of methanol. This feature is drastically modified in the spectrum of methanol adsorbed in HY; it appears to be considerably broadened and reduced in intensity. The authors attributed this change to hydrogen bonding of the methanol OH groups to the zeolite Si(OH)Al groups in HY. For methanol adsorbed in HZSM-5, the OH deformation mode cannot be seen at all in the INS spectra in Fig. 1 (c) and (d), whereas the other modes are similar to those in HY. This difference is suggested to arise from dissociation of methanol in ZSM-5, the water generated being removed in the flowing nitrogen stream used to carry methanol vapour onto the zeolite.

The apparent absence of hydrogen bonded methanol from the INS spectrum of methanol adsorbed in HZSM-5 at room temperature is surprising, given the infrared evidence for hydrogen bonding of methanol [23]. A clear explanation for this disagreement between the two different vibrational spectroscopies is presently lacking and constitutes 'work in progress'. The infrared spectra indicate a considerably stronger hydrogen bond between methanol and the Si(OH)Al groups in ZSM-5

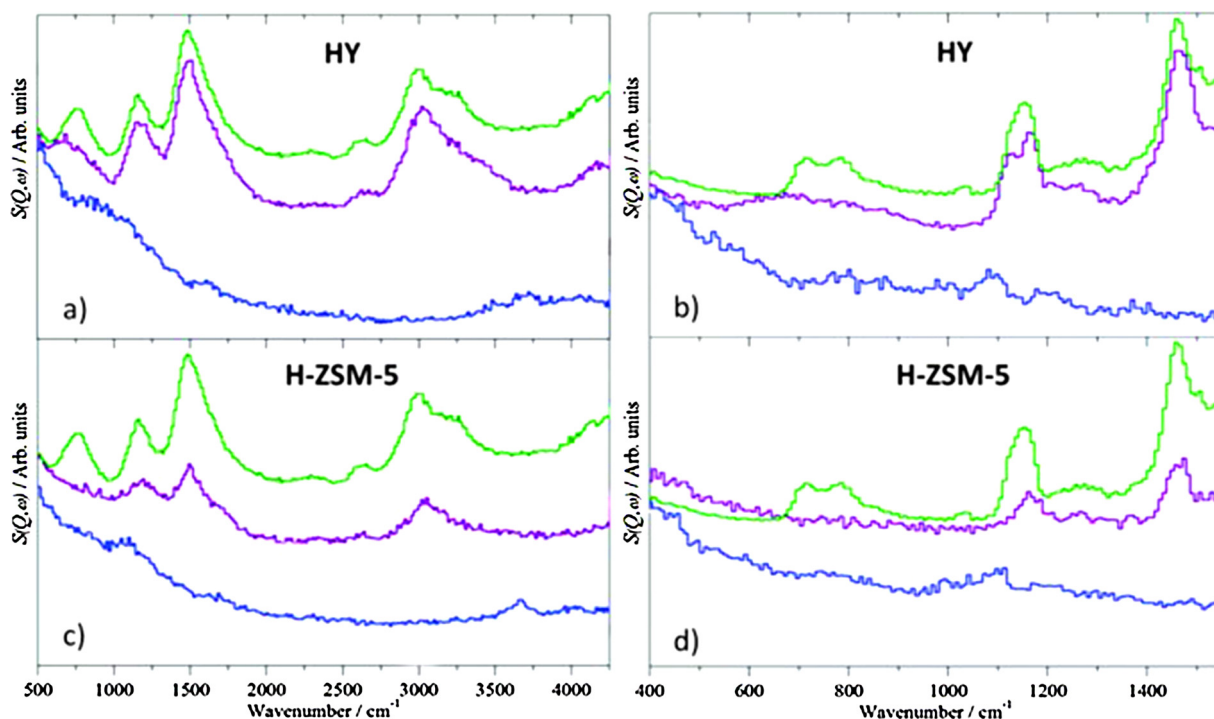
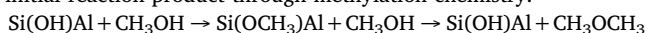


Fig. 1. INS spectra of methanol adsorbed in zeolites HY and HZSM-5 at room temperature. Blue traces (lower) are the blank zeolite, green traces (upper) the spectra of solid methanol, and purple traces (middle) the spectra of methanol adsorbed in the zeolite. (a) zeolite HY, measured on MAPS spectrometer with an incident neutron energy of 5200 cm^{-1} ; (b) zeolite HY measured with an incident energy of 2000 cm^{-1} ; (c) zeolite HZSM-5 measured on MAPS spectrometer with an incident neutron energy of 5200 cm^{-1} ; (d) zeolite HZSM-5 measured with an incident energy of 2000 cm^{-1} . Reproduced with permission from reference [24]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

than in HY. The shift to lower frequency in the zeolite OH stretch as a result of hydrogen bonding is estimated to be about 1200 cm^{-1} for HY and 1600 cm^{-1} for HZSM-5. (the actual infrared spectra show a more complex band structure due to Fermi resonance between the shifted OH stretching mode and overtones of OH deformation modes, as discussed in detail in reference [23]). One possibility is that the OH deformation mode of adsorbed methanol is broadened even further in HZSM-5 than in HY, becoming impossible to detect. The authors of this review are currently attempting to resolve this issue. Although some slight dissociation of methanol may occur at room temperature, it is difficult to accept that the hydrogen bonded methanol detected by infrared spectroscopy would be invisible to INS.

3.2. Methanol in ZSM-5 at reaction temperatures

Infrared spectroscopy [20] indicates that methanol in HZSM-5 dissociates fully to methoxy groups at $200\text{ }^{\circ}\text{C}$ and forms dimethylether as an initial reaction product through methylation chemistry:



To investigate this chemistry by INS, Suwardiyanto et al. [26] used a fixed bed reactor system described in [25] which holds $\sim 12\text{ g}$ of zeolite catalyst in a stainless steel fixed bed reactor connected to a gas feed control allowing methanol (or other reactants) to be passed over the catalyst continually at reaction temperature with on-line mass spectrometric analysis of reaction products and off-line collection of liquid products for later GC–MS analysis. After a given reaction time the catalyst is removed from the reactor and loaded into a sample cell for INS measurement in a high purity argon glove box.

Fig. 2 shows INS spectra from HZSM-5 exposed to methanol at $200\text{ }^{\circ}\text{C}$ for 1 h, measured in the direct MERLIN spectrometer with three different incident neutron energies. At this temperature, the only reaction products detected by MS analysis were dimethylether and water.

At the highest incident energy, (5244 cm^{-1}) the zeolite OH stretching mode at 3600 cm^{-1} cannot be seen, and the intense band at $\sim 3000\text{ cm}^{-1}$ can be assigned to CH stretching modes of surface methoxy groups. The corresponding CH_3 deformation and rocking modes at 1470 and 1180 cm^{-1} respectively are clearly resolved when 2017 cm^{-1} incident energy is used. Unlike the spectra reported in Fig. 1 for methanol in HZSM-5 at room temperature, the 1210 cm^{-1} incident energy spectrum shows weak features $\sim 800\text{--}900\text{ cm}^{-1}$ which may suggest some hydrogen bonded methanol is also present.

At temperatures above $250\text{ }^{\circ}\text{C}$ methanol begins to be converted to hydrocarbons over ZSM-5. Fig. 3 shows mass spectrometer traces from an experiment in which the HZSM-5 catalyst was exposed to a continuous flow of methanol at $350\text{ }^{\circ}\text{C}$ over a 3 day period. The very first product detected is dimethylether (monitored at $m/z = 46$); this declines after $\sim 1\text{ h}$ on stream and olefins propene ($m/z = 41$) and butene

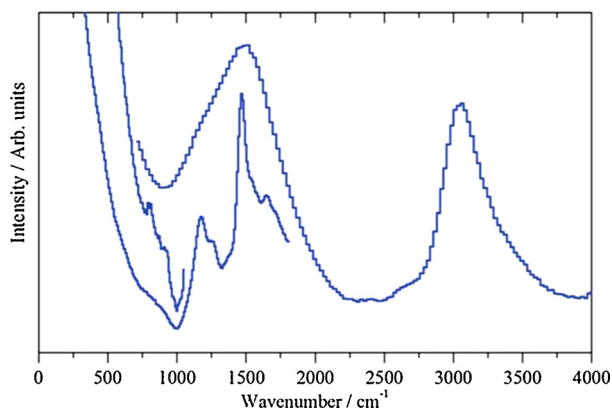


Fig. 2. INS spectra of methanol reacted over HZSM-5 at $200\text{ }^{\circ}\text{C}$ for 1 h. Spectra recorded on the MERLIN spectrometer with incident neutron energies of 5244 , 2017 and 1210 cm^{-1} . Reproduced with permission from reference [26].

($m/z = 55$) are detected, and after a further delay methyl aromatics (monitored by the appearance of the tropylium ion, $m/z = 91$, which is a major fragment formed in the mass spectrometer from methyl aromatic compounds).

It is clear that after the initial break-in period, steady state conversion of methanol to a mixture of alkenes and methyl aromatic products is achieved which is maintained for 3 days. GC–MS analysis of the liquid products collected showed the methyl aromatic products to be a mixture of toluene, dimethyl and trimethyl benzenes with lesser amounts of tetramethylbenzenes and methyl naphthalenes. These reaction profiles are consistent with literature reports of initial break-in and steady state production of olefins and gasoline range hydrocarbons. The novelty of the experiments reported in [25] was the removal of catalysts after different times on stream for analysis by INS (and other spectroscopic and physical measurements).

Fig. 4 shows for example INS spectra from a catalyst taken from the reactor after 1 h on stream at $350\text{ }^{\circ}\text{C}$.

These spectra differ in several important respects from those obtained with methanol at $200\text{ }^{\circ}\text{C}$ (Fig. 2). The amount of hydrocarbons species in the zeolite after reaction at $350\text{ }^{\circ}\text{C}$ for 1 h is quite low (*ex-situ* temperature programmed oxidation measurements estimated about $2.6\text{ wt } \%$ carbon) so the INS spectra are relatively weak. At this temperature, after 1 h of reaction, only a small fraction of the zeolite hydroxyl groups have been lost, as seen in the difference spectra. The CH stretching band at $\sim 3000\text{ cm}^{-1}$ is similar to that seen at $200\text{ }^{\circ}\text{C}$, although much less intense. In the lower frequency region seen with 2017 cm^{-1} excitation energy there are very clear differences from the spectrum at $200\text{ }^{\circ}\text{C}$. (Fig. 2). The bands are much less intense, requiring spectral subtraction to be seen clearly. There is a broad band comprising multiple components between 1350 and 1500 cm^{-1} that is clearly seen in the un-subtracted spectrum. Other features at lower frequency are less clear and only evident in the subtracted spectrum (obscured by the zeolite OH deformation modes).

Infrared and NMR studies of the initial stages of methanol conversion over HZSM-5 have indicated that the first hydrocarbon species containing carbon-carbon bonds formed in the zeolite are oligomers formed from alkenes. [21] Since in the INS work described above alkenes were the major products detected by mass spectrometer analysis during the first hour of reaction at $350\text{ }^{\circ}\text{C}$, alkene oligomers may contribute to the INS spectrum in Fig. 4.

In a separate study, Hawkins et al. measured INS spectra of propene adsorbed in HZSM-5 at various temperatures [27]. At low temperature, the spectrum of adsorbed propene is closely similar to that of the frozen propene gas, but exposure of the zeolite to propene at room temperature (then quenching to 20 K for the INS measurement) gives a spectrum characteristic of a linear long chain polypropene oligomer. Fig. 5 compares this spectrum with that of frozen propene. The concentration of oligomer formed from propene at room temperature is orders of magnitude higher than that seen in the methanol catalyst after 1 h at $300\text{ }^{\circ}\text{C}$ (compare the intensity of the CH stretching bands at 3000 cm^{-1} relative to the OH band of the blank zeolite). In the region $1300\text{--}1500\text{ cm}^{-1}$ the oligomer formed from propene at room temperature shows 3 intense and clearly resolved bands due to bending modes of CH_2 and CH_3 groups. The resolution of the MERLIN spectrometer used to measure the methanol catalyst spectra in Fig. 4 is inferior to that of the MAPS spectrometer used for the more recent measurements in Fig. 5. Nevertheless, this comparison suggests that low concentrations of oligomer species may be present after 1 h of exposure to methanol at $350\text{ }^{\circ}\text{C}$.

The catalytic data in Fig. 3 indicate that steady state production of gasoline range hydrocarbons is occurring after 2 and 3 days on stream at $350\text{ }^{\circ}\text{C}$, consistent with previous studies concluding that the zeolite contains a steady state hydrocarbon pool under these conditions. Fig. 6 shows INS spectra measured with two different direct spectrometers, MAPS and MERLIN, of a catalyst removed from the reactor after 3 days on stream at $350\text{ }^{\circ}\text{C}$.

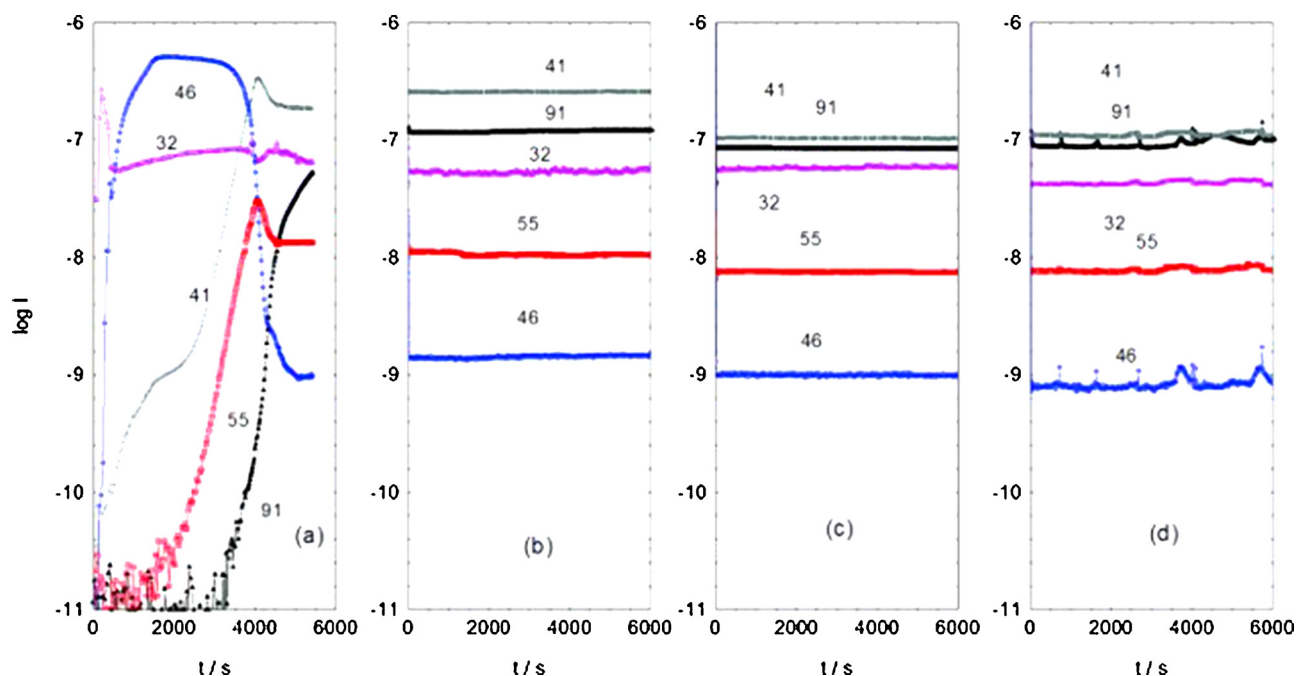


Fig. 3. Reaction product profile from methanol reacted continuously over HZSM-5 for three days at 350 C. (a) initial exposure to methanol, (b) after 1 day, (c) after 2 days, (d) after 3 days. Each frame displays MS data over a 1.7 h period. $m/z = 91$ measures methyl aromatics, $m/z = 55$ butene, $m/z = 46$ dimethylether, $m/z = 41$ propene and $m/z = 32$ methanol. Reproduced with permission from reference [26].

The hydrocarbon content of the zeolite is considerably higher than after 1 h on stream (temperature programmed oxidation indicated 7.1% carbon). This is also obvious from the intensities of the INS bands. Note that the zeolite still contains some residual Si(OH)Al Bronsted acid sites, as seen from the 3600 cm^{-1} band. In the CH stretching region, the MERLIN measurements show a single band at $\sim 3000\text{ cm}^{-1}$ but the higher resolution of the MAPS spectrometer reveals this to have two components, at about 2990 and 3090 cm^{-1} . These were assigned respectively to CH stretching modes of sp^3 hydrocarbon species (CH_3 and CH_2) and to sp^2 hydrocarbon species, i.e. olefinic and/or aromatic species.

Below 1800 cm^{-1} the band at $\sim 1630\text{ cm}^{-1}$ is in the region expected for C–C stretching vibrations of aromatic rings, which will be visible in INS if there is some coupling with CH modes (a pure C–C stretching mode would be effectively invisible to INS). Suwardiyanto et al. assigned the triplet of bands at 1460 , 1390 and 1190 cm^{-1} to asymmetric and symmetric bending modes and rocking mode respectively of methyl groups in methyl aromatic molecules in the hydrocarbon pool, although it was recognised that the hydrocarbon pool in fact comprises a complex mixture of species.

4. Reaction of dimethylether over ZSM-5

As noted above, dimethylether is the first product formed when methanol is passed over ZSM-5 at $200\text{ }^\circ\text{C}$ or above. In Mobil's fixed bed process for making gasoline from methanol the feed into the ZSM-5 reactors is in fact a mixture of methanol and dimethylether (formed by passing methanol over an alumina pre-catalyst bed). Accordingly, Zachariou et al. [28] performed experiments similar to those described above by passing a continuous flow of dimethylether over the catalyst bed then removing catalyst samples for INS analysis.

Fig. 7 shows profiles of reaction products detected by mass spectrometric analysis of the gas stream from the reactor in two different experiments at $350\text{ }^\circ\text{C}$.

In Fig. 7(a), catalyst deactivation begins after ~ 20 h on stream, with a rising concentration of unreacted dimethylether and gradual decline in propene, butene and methyl aromatics. Temperature-

programmed oxidation gave a carbon content of 18.7 wt% after 36 h on stream. In Fig. 7(b), where the dimethylether flow rate was reduced, the deactivation time was correspondingly lengthened, and the carbon content after 75 h on stream was 14.6 wt%. In a third experiment, a catalyst was exposed to dimethylether for 24 h at a WHSV of 0.5, showed no loss of activity during this time and gave a carbon content of 8.8 wt%. GC–MS analysis of the trapped liquid products showed predominantly tetramethyl benzenes, trimethyl benzenes and xylenes [28].

INS spectra of all three catalysts were remarkably similar. Fig. 8 shows spectra measured in the $2000\text{--}4000\text{ cm}^{-1}$ range with the MERLIN spectrometer.

In all 3 cases the zeolite Si(OH)Al stretching mode at 3600 cm^{-1} is totally absent. The CH stretching band has two clear components, at ~ 2990 and $\sim 3100\text{ cm}^{-1}$. As described above for catalysts used in methanol conversion, these are assigned to aliphatic and olefinic/aromatic species respectively.

For these experiments, spectra in the lower frequency region were measured with an indirect geometry instrument, TOSCA. This spectrometer provides for better spectroscopic resolution below 1500 cm^{-1} than that achievable with the direct instruments MAPS and MERLIN. Fig. 9 shows TOSCA spectra of the same three catalyst samples reacted with dimethylether for 1, 2 and 3 days. Although broadly speaking the spectra above 800 cm^{-1} are similar to those shown in Fig. 7 from catalysts reacted with methanol, the superior quality of the TOSCA spectra allows better determination of band positions. The TOSCA instrument also shows clearly the presence of multiple bands down to 200 cm^{-1} which were not resolved in the earlier MAPS and MERLIN spectra of zeolite catalysts.

Assigning all of the bands seen here is a challenging exercise. As a first attempt, Zachariou et al. compared the spectra of the used catalysts with those of plausible methylaromatic compounds which are believed to comprise a large component of the hydrocarbon pool. Fig. 10 shows such a comparison. Above 800 cm^{-1} the used catalyst spectrum more closely resembles that of *o*-xylene than durene, and certainly the presence of aromatic species which are not highly methylated is consistent with the observed profiles of CH stretching bands (Fig. 8). Below 800 cm^{-1} the comparison is not helpful, since the model compounds

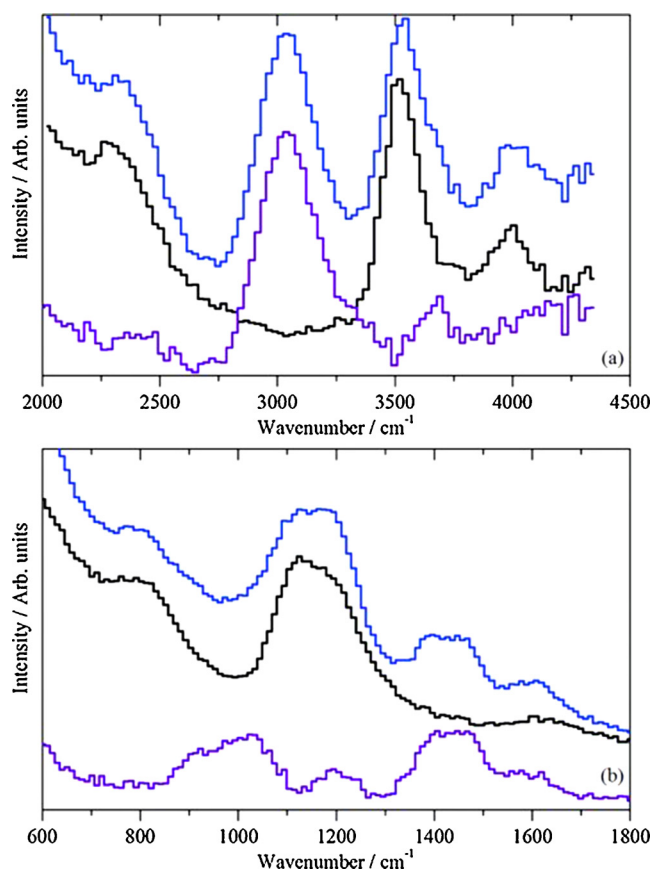


Fig. 4. INS spectra measured with the MERLIN spectrometer of HZSM-5 exposed to methanol at 350 C for 1 h. (a) spectra measured with incident energy 5244 cm^{-1} , (b) spectra measured with incident energy 2017 cm^{-1} . Black traces (middle) are the spectra of the blank dehydrated zeolite, blue (upper) the spectra of the used catalysts and purple (lower) the difference spectra (used catalyst – zeolite blank). Reproduced with permission from reference [26]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

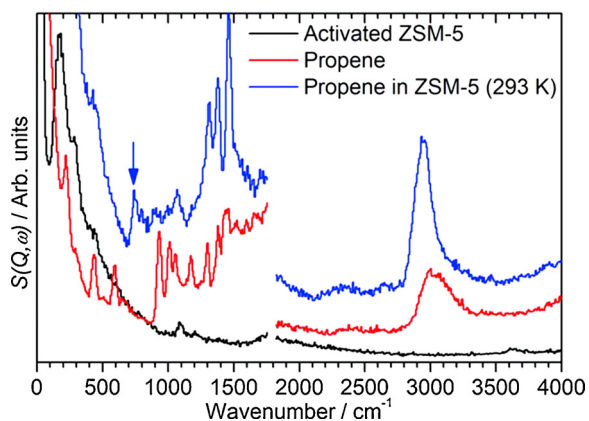


Fig. 5. INS spectra of propene adsorbed in HZSM-5 at room temperature (upper blue trace) compared with pure propene (middle red trace) and the spectrum of the dehydrated zeolite (lower black trace). Spectra measured at 20 K on the MAPS spectrometer with incident frequencies of 5244 cm^{-1} ($2000\text{--}4000\text{ cm}^{-1}$) and 2017 cm^{-1} ($0\text{--}1800\text{ cm}^{-1}$). Arrow marks the 736 cm^{-1} band due to an in-phase rocking mode of CH_2 groups in a linear oligomer. Reproduced with permission from reference [27]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

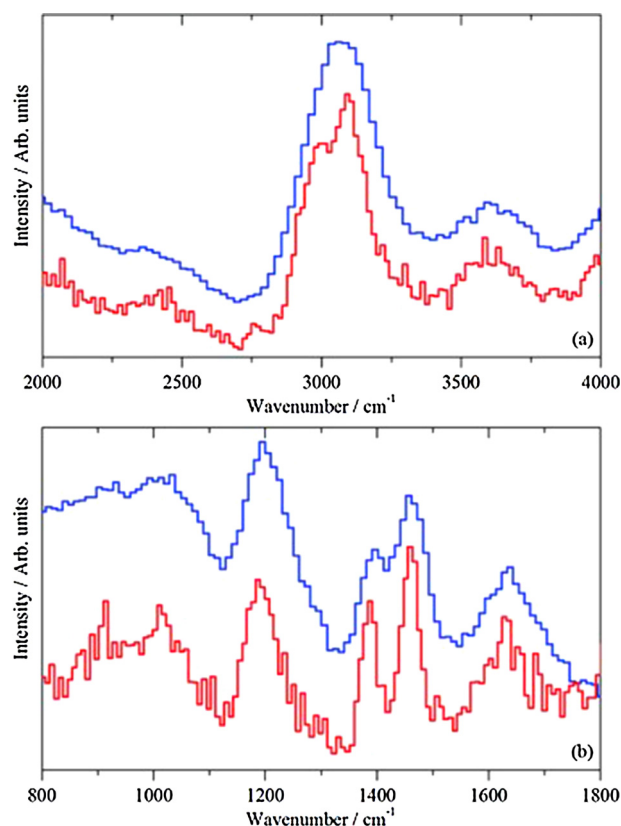


Fig. 6. Spectra measured with the MERLIN (blue, upper) and MAPS (red, lower) spectrometers of ZSM-5 catalyst after reaction with methanol at 350 C for 3 days. Spectra measured at 20 K with incident frequencies of 5244 cm^{-1} ($2000\text{--}4000\text{ cm}^{-1}$) and 2017 cm^{-1} ($800\text{--}1800\text{ cm}^{-1}$). Reproduced with permission from reference [26]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

run as frozen solids will contain lattice and librational modes which will not be found for molecular species adsorbed in the zeolite.

There is no clear difference (other than in intensity) between the active 1 day catalyst and the deactivated 2 and 3 day catalysts, which is consistent with literature suggestions that the initial deactivation is due to the accumulation of methyl aromatic species within the catalyst pores blocking and removing the active acid sites [29], *i.e.* the nature of the hydrocarbon pool in active and initially deactivated catalysts has not changed. Zachariou et al. suggest that the more rapid deactivation seen with dimethylether compared with methanol (Fig. 4) is due to the lower concentrations of water present; importantly this scenario prevents regeneration of the active sites.

5. Concluding remarks

We have reviewed here recently published work showing how INS can provide information about chemistry occurring during conversion of methanol to hydrocarbons over zeolite ZSM-5. INS lacks the spectroscopic resolution of infrared spectroscopy, but can observe all hydrocarbon species present with equal sensitivity. The use of an indirect geometry instrument such as TOSCA in particular opens up opportunities to study in detail the lower frequency vibrational modes which are inaccessible to infrared spectroscopy.

This work is on-going, and we are presently addressing a number of challenges which the experiments described above have raised. These include the following.

- The apparent disagreements between INS and infrared spectroscopy concerning the hydrogen bonding and/or dissociation of methanol

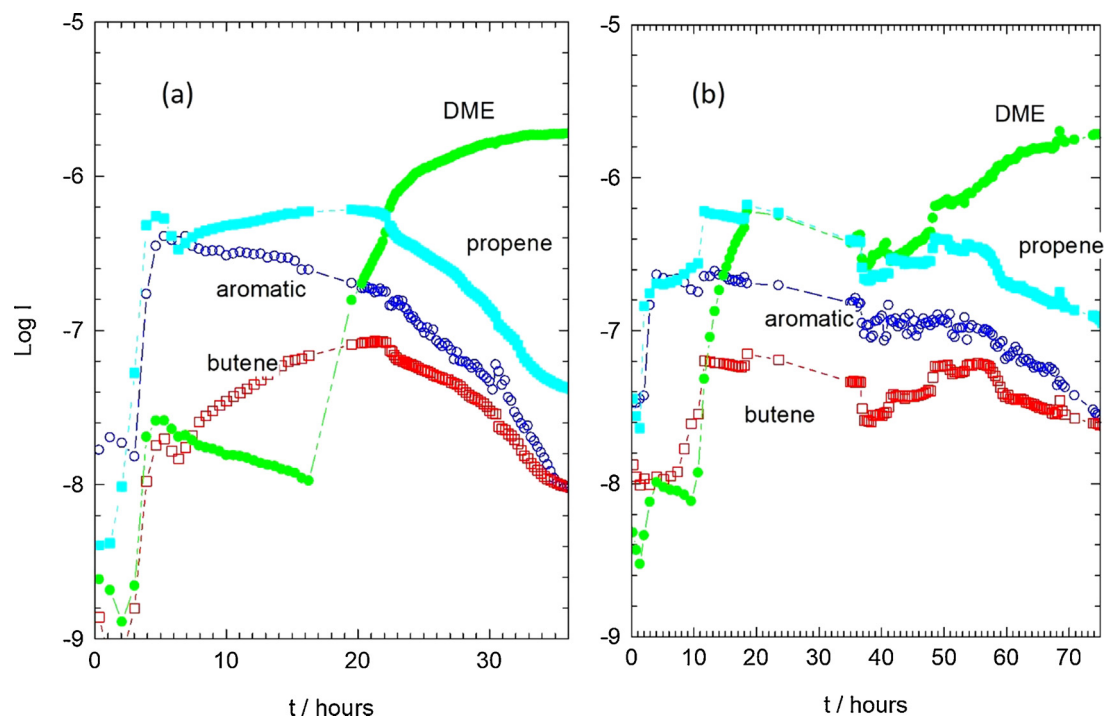


Fig. 7. Mass spectral analysis of evolved gaseous products during DME conversion at 350 °C. (a) 2 day run, WHSV = 0.8; (b), 3 day run, WHSV = 0.3. DME measured as $m/e = 45$, propene $m/e = 41$, butene $m/e = 55$, aromatics as tropylium ion, $m/e = 91$. Reproduced with permission from reference [28].

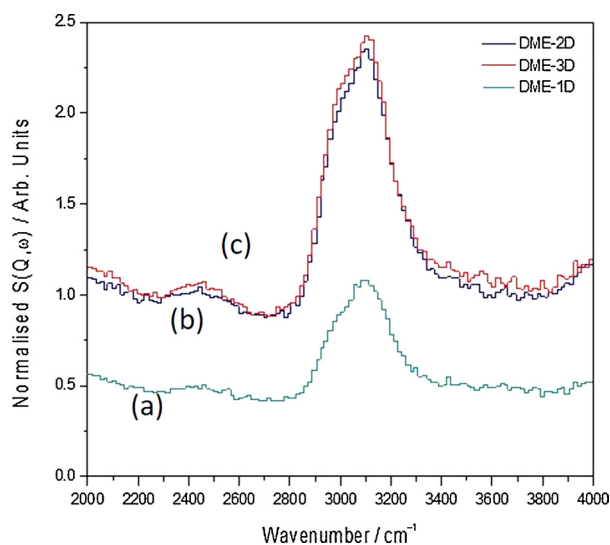


Fig. 8. INS spectra of catalysts reacted with dimethylether for 24 h (1D, (a)), 36 h (2D, (b)) and 75 h (3D, (c)). Reproduced with permission from reference [28].

in acid zeolites at low temperature.

- The analysis of low frequency modes of hydrocarbon species adsorbed in zeolites. As the spectra in Fig. 10 above show, comparisons with spectra of pure compounds, which is an accepted approach for assigning higher frequency bands in both INS and infrared spectroscopy, is not useful below 1000 cm^{-1} . There are two approaches to this problem. One is to adsorb plausible model compounds into the zeolite, and thus identify all intra-molecular vibrational modes of the isolated adsorbed molecules. The other is to employ the now available increasingly sophisticated molecular dynamics simulations to predict the vibrational spectra of intra-zeolitic species over the complete frequency range.
- Signal to noise and scan time remain issues with INS. As noted in the

Introduction, true operando spectroscopy is unlikely to be achieved soon with neutrons but freeze quench experiments, where the measurement cell is used as a reactor at elevated temperatures then quenched to obtain a snapshot of the species present in the catalyst, are presently achievable.

- Finally, a strong selling point of INS is its ability to interrogate industrial catalyst samples without the need for any subsequent sample preparation or treatment, including deactivated samples, and we firmly believe this should be more widely exploited.

CRediT authorship contribution statement

A. Zachariou: Writing - review & editing. A. Hawkins: Writing - review & editing. S.F. Parker: Writing - review & editing. D. Lennon: Funding acquisition. R.F. Howe: Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Johnson Matthey plc and the EPSRC are thanked for postgraduate student support (A.P.H., A.Z.) via the Industrial CASE scheme (EP/P510506/1 and EP/N509176/1 respectively). Johnson Matthey plc is additionally thanked for provision of the ZSM-5 catalyst, plus some characterisation information. The STFC Rutherford Appleton Laboratory is thanked for access to the neutron beam facilities. The UK Catalysis Hub is thanked for resources, support and access to the Research Complex at Harwell which is provided via our membership of the UK Catalysis Hub Consortium and funded by UK Engineering and Physical Sciences Research Council (grants EP/K014706/1, EP/K014668/1, EP/K014854/1, EP/K014714/1 and EP/M013219/1).

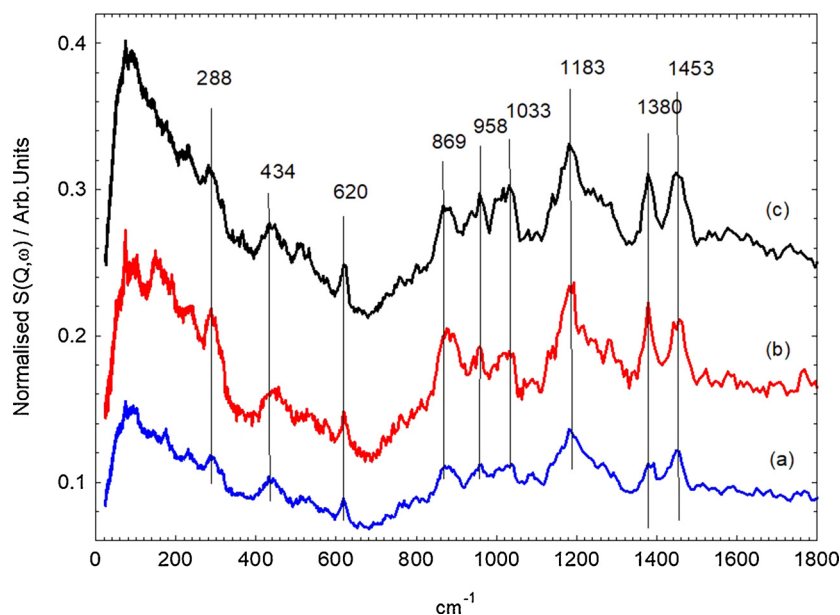


Fig. 9. INS spectra measured on the TOSCA spectrometer of catalysts reacted with dimethylether for 1 day (a), 2 days (b) and 3 days (c). Reproduced with permission from reference [28].

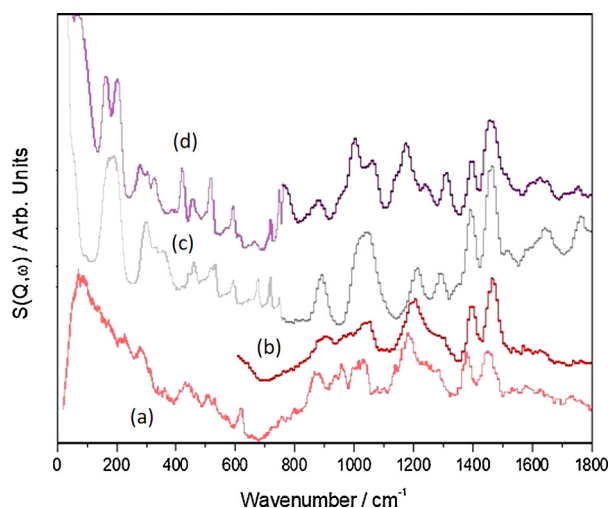


Fig. 10. Comparison of INS spectra of zeolite catalyst reacted with dimethylether for 3 days (TOSCA (a) and MERLIN (b)) with MERLIN spectra of pure p-durene (c) and ortho-xylene (d). Reproduced with permission from reference [28].

References

- [1] F. Zaera, *Chem. Soc. Rev.* 43 (2014) 7624–7663.
- [2] I.E. Wachs, C.A. Roberts, *Chem. Soc. Rev.* 39 (2010) 5002–5017.
- [3] M.J. Wax, R.R. Cavanagh, J.J. Rush, G.D. Stucky, L. Abrams, D.R. Corbin, *J. Phys. Chem.* 90 (1986) 532–534.
- [4] H. Jobic, *J. Catal.* 131 (1991) 289–293.
- [5] H. Jobic, A. Renouprez, A.N. Finch, H.J. Lauter, *J. Chem. Soc. Faraday Trans. 1* 83 (1987) 3199–3295.
- [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] S.F. Parker, D. Lennon, P.W. Albers, *Appl. Spectrosc.* 65 (2011) 1325–1341.
- [8] G.J. Kearley, V.N. Peterson (Eds.), *Neutron Applications in Materials for Energy*, Springer, 2015.
- [9] S.F. Parker, P. Collier, *Johnson Matthey Technol. Rev.* 60 (2016) 132–144.
- [10] P.W. Albers, D. Lennon, S.F. Parker, *Exp. Methods Phys. Sci.* 49 (2017) 279–348.
- [11] A.J. O'Malley, S.F. Parker, C.R.A. Catlow, *Chem. Commun.* 53 (2017) 12164–12176.
- [12] R. Warringham, D. Bellaire, S.F. Parker, J. Taylor, C.M. Goodway, M. Kibble, S.R. Wakefield, M. Jura, M.P. Dudman, R.P. Toozee, P.B. Webb, D. Lennon, *J. Phys. Conf. Ser.* 554 (2014) 012005.
- [13] C.D. Chang, *Catal. Rev. Sci. Eng.* 25 (1983) 1–118.
- [14] S. Xu, Y. Zhi, J. Han, W. Zhang, X. Wu, T. San, Y. Wei, Z. Li, *Adv. Catal.* 61 (2017) 37–122.
- [15] U. Olsbye, S. Svelle, K.P. Lillerud, Z.H. Wei, Y.Y. Chen, J.F. Li, J.G. Wang, W.B. Fan, *Chem. Soc. Rev.* 44 (2015) 7155–7176.
- [16] I. Yarulina, A.D. Chowdhury, F. Meirer, B.M. Weckhuysen, J. Gascon *Nat. Catal.* 1 (2018) 398–411.
- [17] W. Dai, C. Wang, M. Dyballa, G. Wu, N. Guan, L. Li, Z. Xie, M. Hunger, *ACS Catal.* 5 (2015) 317–326.
- [18] E. Borodina, H.S.H. Kamaluddin, F. Meirer, M. Mokhtar, A.M. Asiri, S.A. Al-Thabaiti, S.N. Basahel, J. Ruiz-Martinez, B.M. Weckhuysen, *ACS Catal.* 7 (2017) 5268–5281.
- [19] Y. Ono, T. Mori, *J. Chem. Soc. Faraday Trans. 1* 77 (1981) 2209–2221.
- [20] T.R. Forester, R.F. Howe, *J. Am. Chem. Soc.* 109 (1987) 3076–3082.
- [21] I. Minova, S.K. Matam, A. Greenaway, Suwardiyanto, R.C.A. Catlow, M.D. Frogley, G. Cinque, P.A. Wright, R.F. Howe, *ACS Catal.* 9 (2019) 6564–6570.
- [22] S.K. Matam, R.F. Howe, A. Thetford, C.R.A. Catlow, *Chem. Commun.* 54 (2018) 12875–12878.
- [23] A. Zecchina, S. Bordiga, G. Spoto, D. Scarano, G. Spano, F. Geoboldo, *J. Chem. Soc. Faraday Trans.* 92 (1996) 4863–4875.
- [24] A.J. O'Malley, S.F. Parker, A. Chutia, M.R. Farrow, I.P. Silverwood, V. Garcia-Sakai, C.R.A. Catlow, *Chem. Commun.* 52 (2016) 2897–2900.
- [25] I.P. Silverwood, N.G. Hamilton, A. McFarlane, R.M. Omorod, T. Guidi, J. Bones, M.P. Dudman, C.M. Goodway, M. Kibble, S.F. Parker, D. Lennon, *Rev. Sci. Instrum.* 82 (2011) 034101.
- [26] Suwardiyanto, R.F. Howe, E.K. Gibson, C.R.A. Catlow, A. Hameed, J. McGregor, P. Collier, S.F. Parker, D. Lennon, *Faraday Discuss. Chem. Soc.* 197 (2017) 447–471.
- [27] A.P. Hawkins, A. Zachariou, P. Collier, R.A. Ewings, R.F. Howe, S.F. Parker, D. Lennon, *RSC Adv.* 9 (2019) 18785–18790.
- [28] A. Zachariou, A.P. Hawkins, D. Lennon, S.F. Parker, Suwardiyanto, S.K. Matam, C.R.A. Catlow, P. Collier, A. Hameed, J. McGregor, R.F. Howe, *Appl. Catal. A Gen.* 569 (2019) 1–7.
- [29] D.M. Bibby, R.F. Howe, G.D. McLellan, *Appl. Catal.* 93 (1992) 1–34.