



Technical Information

In-Situ Thermal Analysis MS with the HPR-20 Solid Insertion Probe

Summary

Hidden quadrupole mass-spectrometers are ideal systems for monitoring evolved species from thermal analysis systems. The combination of their high precision manufacture and application specific configurations provide a powerful and flexible tool for the analyst. However even under ideal conditions conventional TA-MS suffers limitations e.g. detection of trace species from very small samples. To address these highly demanding applications Hiden Analytical have developed the HPR-20 Solid Insertion Probe system, an integrated MS with a heatable probe and gas / vapour dosing system to allow the direct analysis of thermal events, in-situ, within the manifold of the MS itself to provide unparalleled response and sensitivity in the analysis of thermal events and gas – solid interactions. This application note illustrates these capabilities with an examination of the influence of shape selectivity in the acid-catalysed reactions of iso-propyl alcohol.

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In-Situ Thermal Analysis-MS

The use of Thermal Analysis – Mass Spectrometry (TA-MS) is commonplace and provides an essential characterisation tool to the materials scientist. Thermal Analysis allows full control of the sample pressure, temperature as well regulation of any gas / vapour treatment stream combined with accurate weight measurement of uptake, desorption or decomposition.

MS compliments this with speciation of all evolved species as a function of time and / or temperature.

However in certain cases TA-MS presents certain limitations e.g. the analysis of trace levels of evolved species, or the ultra-fast analysis of transient species. To address these highly demanding applications Hiden have developed the 'in-situ' TA-MS analyser, the HPR-20 Solid Insertion Probe (HPR-20 SIP) as shown in Figures 1 and 2.

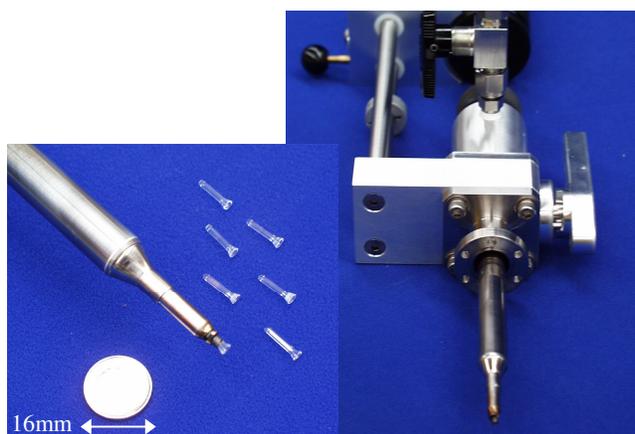


Figure 1. Detail of the Solid Insertion Probe

The HPR-20 SIP consists of a standard HPR-20 atmospheric-sampling MS manifold with QIC inlet modified by incorporation of the Solid Insertion Probe and gas / vapour dosing / sample pre-treatment chamber. The end of the probe arm contains a heater coil into

which the solid sample is placed to provide near-direct heating up to 800°C using linear or ballistic heating modes. The close mounting of the sample to the heater and small sample size both minimise any thermal gradients, while the forced air-cooling through the shaft of the SIP minimises heat transfer to the probe shaft. The isolatable sample preparation chamber (shown in Figure 3) provides for the direct pre-treatment of solid prior to thermal analysis. The pre-treatment chamber resides at vacuum conditions of ca. 10^{-2} – 10^{-3} Torr, facilitated by an independent rotary or membrane pump, to both assist in the desorption of non-interacting species but also to allow sample transfer from atmospheric pressure to UHV conditions. Hence it is possible to degas samples or adsorb gases or vapours onto a sample, in-situ, prior to transfer into the UHV quadrupole housing for 'in-situ' UHV analyses. The presence of the sample in immediate proximity to the quadrupole ioniser provides the user with ultra-fast response and state-of-the-art detection limits.



Figure 2. The HPR-20 SIP

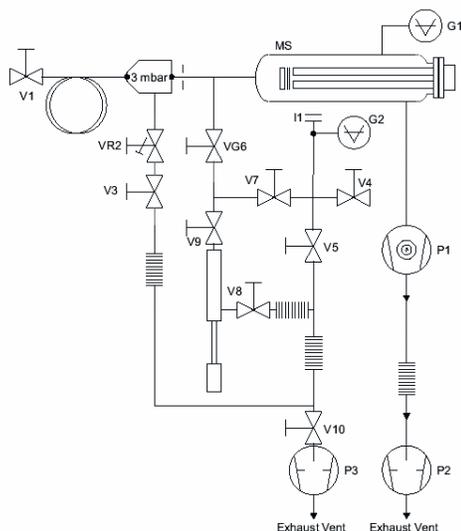


Figure 3. Flow Schematic of the HPR-20 SIP

Initial studies using the SIP addressed the application of $\gamma\text{-Al}_2\text{O}_3$ in simple acid-catalysed reactions. Firstly, a 2mg sample was subjected to a standard temperature programmed desorption (TPD). This involved a preliminary degas and evacuation of ambient residuals in the pre-treatment chamber for 1h prior to transfer to the UHV manifold for in-situ heating at 10 °C / min to 500 °C. Note, the provision of forced-cooling during the temperature ramp was found to assist in obtaining a linear heating rate, due to the small thermal sample mass.

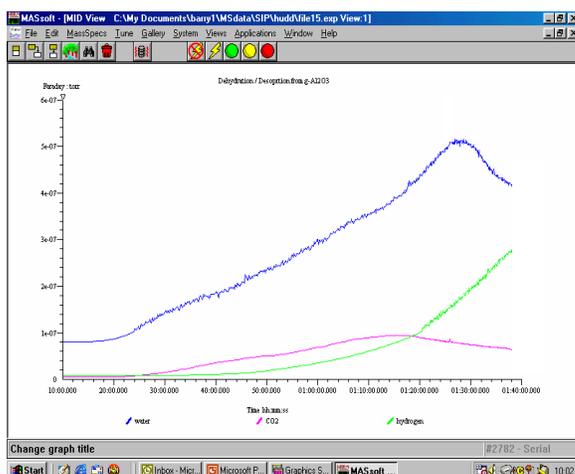


Figure 4 – Dehydration / Degas of $\gamma\text{-Al}_2\text{O}_3$

The resultant TPD showed a series of broad, overlapping water evolution features reflecting the presence of multiple sources of water within the system. These are ascribed to a combination of adsorbed water desorbing at lower temperatures (50-130 °C) and also the dehydroxylation of Brönsted acid Al-OH sites within the alumina responsible for its acidic properties (1) (400-500 °C with a peak at ca. 450 °C). In addition the data also show the evolution of coincident water and CO₂ features, peaking at approximately 380 °C, consistent with the oxidation of adsorbed hydrocarbon species.

The acid characteristics of the Al₂O₃ were then investigated using the temperature-programmed reaction (dehydration) of iso-propanol (IPA). This involved pre-treatment of fresh, degassed Al₂O₃ (1h at room temperature in the pre-treatment manifold to ca. 3*10⁻³ Torr) with 25 ml of IPA vapour in air. The sample was then degassed for a further hour prior to reaction, again to 500 °C at 10 °C/min. In order to obtain full analysis both the production of H₂, H₂O and CO₂ were monitored (Figure 5a) as well as all evolved organics using the MASsoft profile mode (30-60 amu, Figure 5b). Note that from these profile spectra MASsoft can generate a series of multiple ion trends with each ion corresponding to a fragment of a potential reaction product, a full list of which are shown in Table 1. Trend analysis in multiple ion mode gave the results shown in Figure 5c.

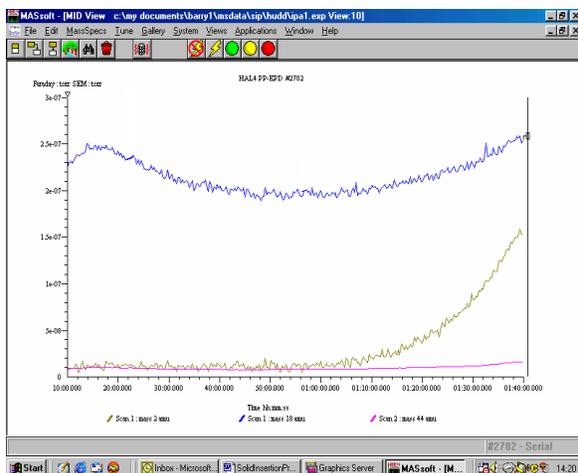


Figure 5a. TPRReaction IPA on $\gamma\text{-Al}_2\text{O}_3$

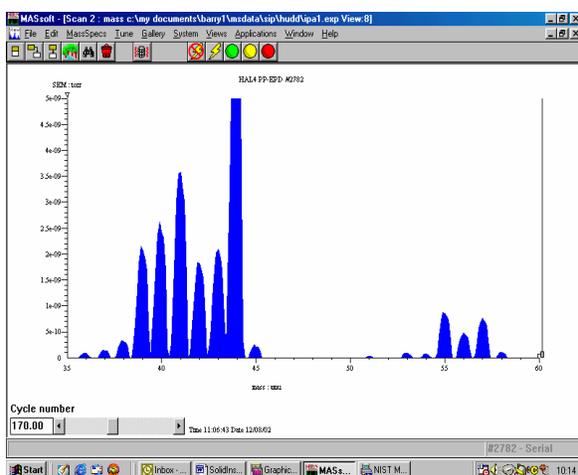


Figure 5b. Profile Scan TPRReaction IPA on $\gamma\text{-Al}_2\text{O}_3$

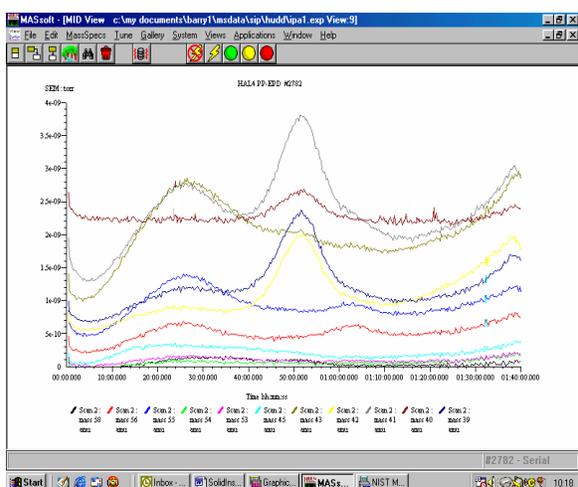


Figure 5c. MID scan TPRReaction of IPA on $\gamma\text{-Al}_2\text{O}_3$

The data obtained reflect a varied set of reactions occurring on the catalyst. However it is possible to deconvolute the extensive fragmentation pattern by comparison of their trends with the expected fragmentation contributions in Table 1. Application of this analysis to the sets of low temperature desorption peaks centred at 140 °C confirm the production of mixed C_6 alkenes, predominantly 2 methyl pent-2-ene, 4 methyl pent-2-ene and hex-1-ene with additional trace levels of 2 methyl pent-1-ene, hex-2-ene. Coincident to this the desorption of low levels of propene was also recorded. These observations are consistent with the acid-catalysed dimerisation of propene monomers (see example in Figure 7b and 2), the latter species arising from the acid-catalysed dehydration of the iso propanol (Figure 7a and 2).

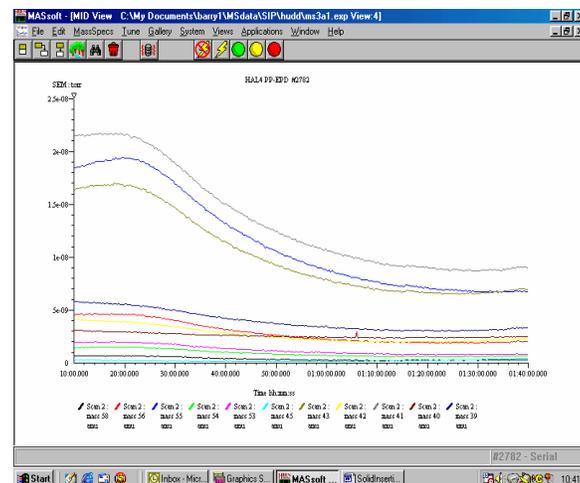


Figure 6. TP Reaction of IPA on Mol sieve 3A

In addition a small desorption maxima was recorded for m/e 45 at 120 °C. This is coincident with water desorption (Figure 5a) and ascribed to a combination of IPA and iso-propyl ether (H₃CHC(CH₃) OCH(CH₃)CH₃), the latter from acid-condensation of IPA. Oxygenate production is also observed at m/e 58, i.e. acetone, which shows small peaks at 175 and 250 °C. This reflects the minor dehydrogenation

function of the Al₂O₃ (3). Finally a set of large coincident peaks at 265 °C with a series of small shoulders at ca. 325 °C were recorded. The main peaks confirm exclusive production of propene, and reflect the presence of strong, homogeneous acid sites, while the shoulder features again suggest the production of C₆ dimers. Further heating resulted in a broad, and non-resolvable features, consistent with extensive dehydration, dimerisation and cracking.

Table 1. Cracking Patterns for Potential Reaction Products in IPA dehydration (4).

Species	Significant Peaks in 30-60 amu range (m/z: % intensity of primary peak)
IPA	45: 99.9 43: 14.2
Acetone	58: 33.1 43: 99.9
Propene	42: 66.3 41: 99.9 40: 29.2 39: 77.3
Iso-propyl ether	45: 99.9 43: 38.9 41: 12.2
Hex-1-ene	56: 85.7 55: 58.7 43: 58.9 42: 74.6 41: 99.9 39: 49.0
Hex-2-ene	56: 25.6 55: 99.9 54: 10.3 53: 11.7 43: 10.7 42: 41.6 41: 43.9 39: 37.2
2 Methyl pent-1-ene	56: 99.9 55: 47.3 53: 11.6 43: 9.9 42: 31.8 41: 89.3 40: 10.8 39: 52.1
2 Methyl pent-2-ene	55: 12.5 41: 99.9 39: 28.8
4 Methyl pent-2-ene	56: 44.0 43: 99.9 42: 33.2 41: 72.2 39: 30.8

These data are consistent are consistent with previous studies (3) and may be contrasted with the activity observed in the case of a 'shape selective' acid catalyst, in this case Molecular Sieve 3A. Mol Sieve 3A has a Zeolite A (Linde Type A, Figure 8) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes. The pore diameter is defined by an 8 member oxygen ring and is small at 4.2Å, although in 3A this

is further reduced by ion exchange of the sodium ion for potassium, giving an effective diameter of 3Å. This endows the material with its 'shape selective' characteristics due to the exclusion of molecules with a critical diameter of > 3Å. This had led to commercial application in household detergents to ion exchange Calcium and Magnesium from 'hard water' and industrially to dry solvents e.g. methanol.

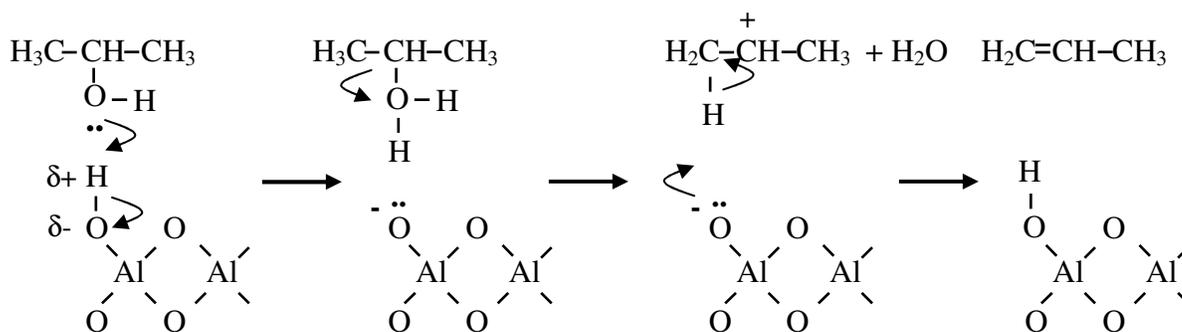


Figure 7a Reaction Mechanism of the Acid Catalysed Dehydration of IPA

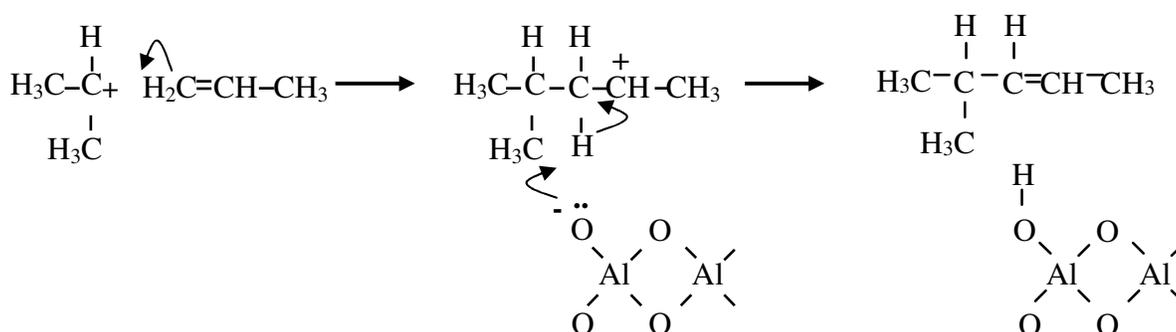


Figure 7b. Acid-Catalysed dimerisation of Propene to 4-methyl pent-2-ene

The shape selective characteristics are also demonstrated in Figure 6 for the TP Reaction of IPA on Mol Sieve 3A. Catalyst pre-treatment and ramp rate were identical to those employed previously. However the performance of the sample is radically different to the standard Al_2O_3 . Instead of the multiplicity of peaks occurring throughout the temperature range the sample only displays a broad low temperature desorption of mixed C6 isomers, coincident with a broad desorption of water, again centred at ca. 120 °C. This is indicative of the reaction of loosely bound species on the external surface of the catalyst, consistent with the shape selective

nature of the catalyst excluding the IPA molecule from the pore structure (the critical diameter of IPA $\gg 3\text{Å}$) and the majority of the active Brønsted acid centres within the framework structure.

Conclusions.

Hiden Analytical have developed the HPR-20 Solid Insertion Probe system for 'in-situ' thermal analysis studies with state-of-the-art sensitivity and response. Initial studies using the HPR-20 SIP have examined the acid-catalysed reactions of iso-propyl alcohol over γ -Al₂O₃ and Mol Sieve 3A. The former yielded a diverse range of dehydration, dehydrogenation and dimerisation products, which all reactions displaying individual temperature dependences. In contrast, a limited set of low temperature reactions were observed over the Mol Sieve catalyst, the differences in reactivity being linked to reactant shape selectivity limiting access of the IPA reagent to the active internal acid sites.