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Dynamic Nuclear Polarization Solid-State NMR in Heterogeneous Catalysis Research

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1. INTRODUCTION

A revolution in solid-state nuclear magnetic resonance (SSNMR) spectroscopy is taking place, attributable to the rapid development of high-field dynamic nuclear polarization (DNP), a technique yielding sensitivity improvements of 2–3 orders of magnitude. This higher sensitivity in SSNMR has already impacted materials research, and the implications of new methods on catalytic sciences are expected to be profound.

With their unique sensitivity to the local electronic environment, the nuclear spins can play the role of perfect reporters in the quest for a fundamental understanding of the catalytic processes at the atomic-scale. Indeed, during the last several decades, SSNMR spectroscopy has evolved to become one of the premier analytical methods for structural characterization of heterogeneous catalytic systems, providing in-depth knowledge about catalyst supports, active sites, reacting molecules, and their interactions.1–3 Noteworthy is also NMR’s ability to investigate a wide range of dynamic processes at solid–liquid and solid–gas interfaces under catalytically relevant pressures and temperatures. The development of sophisticated SSNMR instrumentation, methodology, and advances in theory have endowed the researchers with an ever increasing ability not only to identify and quantify individual chemical sites but also to determine the three-dimensional (3D) catalytic structures, which are often non-periodic and disordered. Of importance are also the active site distribution and the interactions between these sites and the reacting molecules. This area of multidimensional correlation NMR spectroscopy can open new frontiers for the definite characterization of increasingly complex catalytic materials, provided that the issue of low sensitivity can be overcome.

The intrinsically low sensitivity of NMR spectroscopy, which operates at the lowest-energy end of the electromagnetic spectrum, poses the fundamental challenge for catalytic applications, where fast detection of small quantities of nuclei is essential. The traditional remedies for NMR’s sensitivity woes include advances in magnet and probe technologies (e.g., cryoprobes, probes capable of ultrafast magic angle spinning, MAS, low-temperature (LT)MAS probes, or probes for in situ studies), isotope enrichment, the use of large sample sizes, the development of new pulse sequences, as well as improvements in data acquisition and processing protocols.

As briefly mentioned, a newly accessible strategy for increasing the polarization of nuclear spins, DNP, can offer unparalleled enhancements of SSNMR signals, and even greater savings in experimental time of 4–5 orders of magnitude. By enabling the detection of insensitive nuclei, short-lived intermediates, or minute concentrations of molecules and the examination of much smaller surfaces than possible using conventional CP MAS methods, DNP SSNMR is poised to significantly impact materials research. In the following, we wish to briefly highlight some of the new opportunities that DNP SSNMR brings to the field of catalysis.

2. DNP SSNMR

A common strategy used in NMR for signal enhancement involves the polarization of the observed nuclei via more sensitive spins possessing larger gyromagnetic ratios \( \gamma \). The resulting signal enhancement is determined by the relative sizes of the Zeeman interaction for the excited and observed spins, i.e., by a factor of \( \epsilon = \gamma_{\text{exc}}/\gamma_{\text{obs}} \). In conventional SSNMR, this strategy is commonly applied to enhance the polarization of lower-\( \gamma \) nuclei (such as \(^{13}\text{C} \) or \(^{15}\text{N} \)) via cross-polarization under MAS conditions (CPMAS), resulting in signal-to-noise ratio \((S/N)\) enhancements per scan of \( \epsilon = \gamma_{1\text{H}}/\gamma_{1\text{C}} \approx 4 \) or \( \gamma_{1\text{H}}/\gamma_{1\text{SN}} \approx 10 \). Clearly, given the electron’s much larger \( \gamma \), considerably higher \( \epsilon \) values can be achieved by applying a similar principle to the electron–nucleus spin pairs; this is the basic idea behind DNP. Such hyperpolarization of nuclear spins can potentially elicit NMR signal enhancements of \( \epsilon = \gamma_{\text{el}}/\gamma_{1\text{H}} \approx 660 \) or \( \gamma_{\text{el}}/\gamma_{1\text{SN}} \approx 6500 \), which translates to time savings of \((660)^2 \) and \((6500)^2 \), respectively. In practice, the technique relies upon saturation of the electron paramagnetic resonance (EPR) line of unpaired electrons by microwave (MW) irradiation and subsequent transfer of polarization to the material’s nuclei of interest. Of key importance is the improvement in \( S/N \) per unit of experimental time, given by \( \epsilon_{\text{time}} = (\gamma_{\text{exc}}/\gamma_{\text{obs}})(T_{1\text{obs}}/T_{1\text{exc}})^{1/2} = \epsilon(T_{1\text{obs}}/T_{1\text{exc}})^{1/2} \), where \( T_{1\text{obs}} \) and \( T_{1\text{exc}} \) denote longitudinal relaxation times of the observed and excited nuclei, which often, but not always, increase at lower temperatures.

The DNP effect was predicted by Overhauser6 and confirmed experimentally by Slichter7 in the early 1950s. The mechanism at play in those studies is known as the Overhauser effect; however, several other DNP mechanisms were subsequently demonstrated, including the solid effect,8,9 thermal mixing10,11 and the cross-effect.11–15 Still, for several decades, the technique remained in a “dormant state”, hindered by the lack of suitable technology compatible with high-field NMR instruments.16 The turnaround is mainly attributable to Griffin and his co-workers who, during the past decade, have brought high-field DNP SSNMR to prominence by the combined development and implementation of advanced gyotron technology,17,18 low-temperature MAS probes,19,20 and...
and improved polarizing agents.\textsuperscript{21–24} The progress in DNP instrumentation and methodology has been scrutinized in several excellent reviews.\textsuperscript{16,25–27} In short, current state-of-the-art DNP in solids requires the use of exogenous biradical polarizing agents for which the EPR frequencies of the two unpaired electrons differ roughly by the nuclear Larmor frequency. This EPR frequency separation facilitates DNP by matching the condition for an efficient three-spin polarization exchange involving two unpaired electrons and a nucleus, known as the cross-effect. Measurements involving the detection of low-\(\gamma\) nuclei can be carried out using a single polarization step: electron \(\rightarrow\) low-\(\gamma\) nucleus (referred to as direct DNP) or, more commonly, via protons with the use of a CP transfer: electron \(\rightarrow\) \(1H\) \(\rightarrow\) low-\(\gamma\) nucleus (indirect DNP). Direct DNP typically leads to lower sensitivity enhancements due to the increased destructive interference between positive and negative DNP enhancement conditions and the more difficult to satisfy cross-effect condition in lower-\(\gamma\) nuclei. Direct DNP does, however, offer theoretically higher enhancements and simplifies the experimental methodology, particularly for quadrupolar nuclei. Promising developments have been made in recent years toward efficient direct DNP using trityl radicals.\textsuperscript{28,29} It should be noted that the DNP transfer step is most efficient at low temperatures, and therefore, most experiments are presently carried out at temperatures not exceeding 110 K.

Whereas challenges remain in developing instrumentation and optimal sample formulations to approach the theoretical limits for \(\epsilon\) in various classes of materials, the capabilities of DNP SSNMR have already proved revolutionary in several areas of research, with initial efforts being focused on biological systems. Importantly for catalysis, Emsley and others have demonstrated the utility of DNP in the studies of mesoporous silica nanoparticles (MSNs) and metal–organic frameworks (MOFs), using the approach termed DNP surface-enhanced NMR spectroscopy (DNP-SENS).\textsuperscript{30–35} Examples are shown in Figure 1, which depicts DNP-SENS \(^{13}C\{^{1}H\}\) and \(^{15}N\{^{1}H\}\) CPMAS spectra of several functional groups deposited at natural isotopic abundance on the surface of mesoporous silica.\textsuperscript{34} The spectra were acquired in 10 min for \(^{13}C\) and 3.5 h for \(^{15}N\) using the bCTbK biradical dissolved in a 1,1,2,2-tetrachloroethane solution, which yielded \(\epsilon\) values on the order of 80. The best currently known polarizing agents for DNP-SENS are the bulky nitroxide biradicals referred to as TEKPol and AMUPol,\textsuperscript{23,24} which under favorable conditions can afford \(\epsilon\) values of over 200. At present, these conditions include a moderate strength of the magnetic field (e.g., 9.4 T) and a low temperature (\(\leq 110\) K), and apply to samples in which the radicals can be administered sufficiently close to the observed nuclei (within tens or hundreds of nm). The indirect DNP experiments require that the spin system comprises a sufficiently dense network of dipolar coupled \(1H\) spins (either intrinsic in the sample and/or in the solvent) to enable efficient transport of enhanced \(1H\) polarization to the nuclei of interest.\textsuperscript{36,37} The samples of catalytic material are typically prepared by wetting the surfaces with a solution of the biradicals in a glass-forming medium to prevent agglomeration of polarizing agents. For TEKPol, which is currently the top performing radical, this involves the use of a 16 mM solution in 1,1,2,2-tetrachloroethane. In general, however, a solvent in which the sample is insoluble should be used and solvents possessing methyl groups should be avoided.\textsuperscript{38} The global sensitivity enhancements offered by DNP, which are determined by the above-mentioned changes in \(T_1\) relaxation, quenching of NMR response by paramagnetic effects (typically on the order of tens of \%), the presence of frozen solvent, changes in the efficiency of cross-polarization, and other experimental factors, strongly vary between different samples. A

Figure 1. DNP-enhanced \(^{13}C\{^{1}H\}\) (B) and \(^{15}N\{^{1}H\}\) (C) CPMAS spectra of hybrid organic–inorganic silica materials decorated with several catalytic precursors (A) under natural \(^{13}C\) and \(^{15}N\) abundance. Adapted with permission from ref 34.
systematic analysis of these contributions for functionalized mesoporous silica material can be found in ref 35.

Importantly, Bruker has recently developed commercial DNP SSNMR instruments operated at 9.4, 14.1, and 18.8 T, with the corresponding gyrotron accessories at 263, 395, and 527 GHz, respectively. One of the first such spectrometers dedicated to materials research has been installed in 2014 at the Ames Laboratory (Figure 2A). The conventional (“MW off”) and DNP-enhanced (“MW on”) 13C{1H} CPMAS spectra of a standard reference sample (proline, Figure 2B) exemplify the highest enhancement ($\epsilon \approx 260$) that can be achieved at 100 K, at least currently, by using AMUPol as a polarizing agent. The instrument uses the lowest of the fields listed above (9.4 T), which at present appears to be the field of choice for DNP applications in catalysis. This point is illustrated in Figure 3, where we compare the 13C{1H} DNP CPMAS spectra taken back-to-back on 9.4 and 14.1 T instruments for the same sample (MSN material functionalized with 3-(N-phenylureido)-propyl groups, denoted as PUP-MSN) under identical conditions: MAS rate $\nu_R = 10$ kHz, $T = 100$ K, and acquisition time $= 11$ min per spectrum. We make several key observations: (1) The spectra exhibit field-independent resolution due to inhomogeneous line broadening. Inhomogeneous broadening is typically encountered in noncrystalline solids due to local disorder, and it lowers the magnetic field dependence of the S/N ratio from $(B_0)^{3/2}$ to $B_0$. (2) In the high-field spectrum (Figure 3B), the intensities are distributed within the manifolds of intense MAS sidebands (denoted as “*”), which interfere with other isotropic resonances. The lower-field spectrum displays minimal interference. (3) Most importantly, the enhancement factor $\epsilon$ at 9.4 T is twice as high than at 14.1 T. This is expected: since the line width of the EPR spectrum increases with $B_0$, the degeneracy condition between the three-spin states involved in the cross-effect becomes more difficult to satisfy at higher magnetic fields. (4) Lastly, the 9.4 T instrument is considerably less expensive. We should also note that the development of improved polarizing agents, MAS capabilities, and optimization schemes will undoubtedly result in higher sensitivity gains at both low and high fields; consider, for example, that the $\epsilon$ values reported in Figure 3 have already been far surpassed by the improved polarizing agents: bCTbK, TEKPol, and AMUPol.

3. DNP SSNMR OF CHALLENGING NUCLEI

One of the major avenues that DNP enables is the study of unreceptive nuclei, such as $^{15}$N, $^{17}$O, $^{35}$Cl, $^{43}$Ca, $^{89}$Y, and $^{119}$Sn. Due to the difficulties in studying these nuclides, which may stem from low natural abundance, low value of $\gamma$, broad lineshapes, or any combination of these factors, they are often referred to as “exotic”; although, with DNP, this terminology may soon become obsolete.

For example, one of the most ubiquitous elements in chemistry and materials science, yet one of the most challenging elements for spectroscopic investigation by NMR, is oxygen. More than 99.96% of oxygen nuclei are NMR silent, and the scarce NMR active isotope ($^{17}$O) has a low g-magnetic ratio ($\gamma_{17O}/\gamma_{1H} \approx 7.4$), a spin of 5/2 and a moderate quadrupole moment ($Q = -25.58$ mb). The second-
order quadrupolar interaction prominently affects most $^{17}$O NMR spectra, because the bonding of oxygen atoms in many solids produces strong electric field gradients at the nuclei, thereby broadening the NMR lines and further reducing the sensitivity. These properties make the use of DNP particularly attractive. Indeed, in spite of all of these shortcomings, DNP-enhanced NMR spectroscopy has enabled the measurement of $^{17}$O NMR spectra at natural isotopic abundance. For example, DNP-enhanced, natural abundance, $^{17}$O{1H} MAS spectra of inorganic hydroxides were recently obtained in our laboratory, enabling the swift measurements of O–H distances and heteronuclear correlation (HETCOR) spectra. Remarkably, DNP has also enabled us to measure the first $^{17}$O spectra of surface hydroxyl groups in natural-abundance silica (Figure 4A). Further improvements in sensitivity will undoubtedly enable the measurement of multidimensional $^{17}$O NMR data of surfaces and allow the site-specific characterization of supported catalysts and host–guest interactions at natural abundance.

Nitrogen, which is also ubiquitous in materials, including catalysts, is similarly indisposed to NMR studies. $^{14}$N NMR spectra suffer from low sensitivity ($\gamma_{1H}/\gamma_{14N} \approx 10$) and low natural abundance (0.37%). Although a > 10-fold boost in sensitivity has been afforded by an indirect detection of low-$\gamma$ $^{15}$N nuclei through high-$\gamma$ $^1$H nuclei, such improvement is often insufficient for the acquisition of $^{15}$N spectra of catalytic surfaces or bulk materials with low nitrogen content. The use of DNP SSNMR enabled the measurement of 1D as well as 2D $^{15}$N spectra of naturally abundant catalytic species within a reasonable experimental time. For example, $^{15}$N DNP SSNMR measurements made it possible to monitor the chemical reactions on functionalized mesoporous silica surface. In another study, DNP-enhanced $^1$H–$^{15}$N HETCOR spectra of Pt2+-loaded metal–organic frameworks (UiO-66-NH2) provided direct evidence of host–guest interactions between Pt2+ and $\text{NH}_2$ groups in UiO-66-NH2 (Figure 4D). Within this virtual special issue, we also report that commonly-used DNP conditions are compatible with the studies of surface-grafted organotransition metal complexes, such as catalytically active zirconium dimethylamide groups. Most recently, spectra of other traditionally challenging nuclei were recorded using DNP, including $^{59}$Co MAS spectra of nitrogen, $^{15}$N, also incurs poor sensitivity, in this case due to the low gyromagnetic ratio ($\gamma_{1H}/\gamma_{15N} \approx 10$) and low natural abundance (0.37%). Although a > 10-fold boost in sensitivity has been afforded by an indirect detection of low-$\gamma$ $^{15}$N nuclei through high-$\gamma$ $^1$H nuclei, such improvement is often insufficient for the acquisition of $^{15}$N spectra of catalytic surfaces or bulk materials with low nitrogen content. The use of DNP SSNMR enabled the measurement of 1D as well as 2D $^{15}$N spectra of naturally abundant catalytic species within a reasonable experimental time. For example, $^{15}$N DNP SSNMR measurements made it possible to monitor the chemical reactions on functionalized mesoporous silica surface. In another study, DNP-enhanced $^1$H–$^{15}$N HETCOR spectra of Pt2+-loaded metal–organic frameworks (UiO-66-NH2) provided direct evidence of host–guest interactions between Pt2+ and $\text{NH}_2$ groups in UiO-66-NH2 (Figure 4D). Within this virtual special issue, we also report that commonly-used DNP conditions are compatible with the studies of surface-grafted organotransition metal complexes, such as catalytically active zirconium dimethylamide groups. Most recently, spectra of other traditionally challenging nuclei were recorded using DNP, including $^{59}$Co MAS spectra of...
in a paramagnetically doped inorganic crystalline lattice,
\( ^{119}\text{Sn}(\text{H}) \) CPMAS and 2D \( ^{1}H-^{197}\text{Sn} \) HETCOR spectra of silica-bound surface complexes and Sn-Beta zeolites (Figure 4B),\(^{49,50} \) as well as Sn/SnO nanoparticles,\(^{51} \) \( ^{89}\text{Y}(\text{H}) \) CPMAS and 2D \( ^{1}H-^{187}\text{Y} \) HETCOR study of hydrated yttrium doped barium zirconate (Figure 4C),\(^{52} \) and wide-line, still unpublished, \( ^{195}\text{Pt} \) spectra of Pt\(^{2+} \)-loaded MOFs in our laboratory.

The range of nuclei amenable to DNP SSNMR will undoubtedly expand in the near future through further advances in instrumentation and pulse sequences, and the development of tailored sample formulations.

4. CHALLENGING SSNMR EXPERIMENTS

Aside from enabling the studies of rare or unreceptive nuclei, DNP also greatly facilitates the implementation of challenging experiments. The acquisition of conventional 2D homo- or heteronuclear correlation spectra is often unfeasible on catalytic systems without isotope enrichment. However, signal enhancements of over 100 approach the benefits obtained from moderate isotopic enrichment when performing \( ^{13}\text{C}-^{13}\text{C} \) homonuclear correlation experiments, while avoiding the complicated, time-consuming, and expensive syntheses associated with labeling. Several reports effectively show that \( ^{13}\text{C}-^{13}\text{C} \) through-space or through-bond 2D spectra can be acquired in a few minutes to hours.\(^{53–56} \) An added benefit of natural abundance measurements is that the 3-spin recoupling effects and dipolar truncation are essentially absent, and carbon–carbon distances may be straightforwardly measured by assuming isolated spin pairs.\(^{57} \) Similarly, \( ^{29}\text{Si}-^{29}\text{Si} \) correlation experiments of the surfaces of functionalized silica nanoparticles have been performed at natural isotopic abundance using DNP.\(^{58} \) These experiments will enable studies of the spatial distributions of species on catalyst’s surface. The sensitivity improvements afforded by DNP will also undoubtedly lead to the detection of \( ^{13}\text{C}-^{15}\text{N} \) correlations at natural isotopic abundance in the near future (corresponding to only 0.004% of carbon–nitrogen bonding partners). Note that with an enhancement factor of 260, which can already be obtained using the AMUPol biradical, see Figure 2B,\(^{24} \) a natural abundance \( ^{13}\text{C}-^{15}\text{N} \) correlation experiment would have comparable sensitivity to a conventional \( ^{13}\text{C}(\text{H}) \) CPMAS experiment.

Correlation experiments involving quadrupolar nuclei, which have low sensitivity due to the quadrupolar spins’ fastidious response to rf pulses, can also be significantly aided using DNP. For example, homonuclear \( ^{27}\text{Al}-^{27}\text{Al} \),\(^{59,60} \) as well as heteronuclear \( ^{13}\text{C}-^{27}\text{Al} \) and \( ^{29}\text{Si}-^{27}\text{Al} \) correlation experiments can be performed in only a few hours. Furthermore, carbon–nitrogen correlation experiments can be performed at natural isotopic abundance in under an hour to a few hours on amino acids by detecting the \( ^{13}\text{C}\text{s} \) correlation to the overtone transition of \( ^{14}\text{N} \).\(^{63} \) Further improvements are expected with

Figure 5. Examples of DNP-enhanced 2D \( ^{13}\text{C}-^{13}\text{C} \) correlation SSNMR spectroscopy. (A) Single-quantum spin diffusion spectrum of methionine and the low-coverage products of its oxidative breakdown on Al\(_{2}\)O\(_3\)-supported Pd nanoparticle catalyst; the cross-peaks are identified on the scheme to the right where circles identify the points of oxidation and/or breakdown responsible for a given cross-peak (blue in (A) corresponds to unreacted methionine). (B), (C) Double-quantum single-quantum MAS spectra of natural abundance microcrystalline cellulose obtained using 1 ms (B) and 3.5 ms (C) of Post-C7 recoupling. Figures (B) and (C) are reproduced with permission from ref 53.
the development of ultrahigh field DNP, offering additional exciting prospects for studying the quadrupolar nuclei in catalytic systems.

5. NOVEL APPLICATIONS OFFERED BY DNP SSNMR

The emergence of modern DNP redefines the sensitivity limits of SSNMR spectroscopy and opens first-time opportunities for the structural studies of bulk materials, molecular structures, and reactions on exceedingly small catalytic surfaces.

The previously mentioned DNP-SENS approach is now being used to examine materials with progressively smaller surface areas that are beyond the current capabilities of conventional NMR methods. For example, DNP-enhanced $^{13}$C/$^1$H CPMAS experiments enabled the detection of signals from $^{13}$C-enriched sucrose adsorbed on low-surface-area (~1 m$^2$/g) hydrated tricalcium silicates. In our laboratory, we recently used DNP to study molecules reacting on the surface of alumina-supported Pd nanoparticle catalyst. Here, DNP offered >2500-fold time-savings, enabling the detection of 2D $^{13}$C–$^{13}$C spin diffusion (Figure 5A) and INADEQUATE spectra of low-coverage products from oxidative degradation of $^{13}$C-enriched methionine adsorbed on the Pd surface.55 To the best of our knowledge, this is the first DNP SSNMR study involving catalytic chemistry at the surface of noble metals, which should inspire further similar investigations in this broad area of catalysis. In another study, the DNP-enhanced $^{29}$Si/$^1$H CPMAS spectra of a trace amount of Si catalytic species obtained, but can also be applied to bulk materials. $^1$H spin diffusion has been shown, both numerically and experimentally, to lead to the efficient hyperpolarization of the bulk nuclei within microcrystals with diameters on the order of tens of microns. This is particularly noteworthy for studying the feedstocks and byproducts of catalytic transformations. See, for example, Figure 5B,C, showing the natural abundance $^{13}$C–$^{13}$C double-quantum correlation spectra of cellulose, in which all expected one-bond (spectrum (B), acquired in only 20 min) and one- and two-bond (spectrum (C), acquired in 2 h) correlation peaks are well resolved.53

- SUMMARY AND OUTLOOK

The hyperpolarization of nuclear spins by DNP forces us to rethink what is possible with SSNMR; note that in many of the studies shown above the DNP spectra acquired within 1 h would require ~2 years of experimental time on a conventional spectrometer. This unprecedented shift in SSNMR’s capabilities offers new opportunities for applications in heterogeneous catalytic systems, which include studies of small surfaces (i.e., materials with surface areas of <1 m$^2$/g), “unreactive” spin-1/2 and quadrupolar nuclei (e.g., $^{15}$N or $^{17}$O in organometallic catalytic groups under natural abundance), elusive intermediates, low-coverage species, and so forth. In spite of these achievements, DNP is still an emerging technology with a large amount of untapped potential. New frontiers in sensitivity will undoubtedly be opened through further, foreseeable or not imagined, advances in DNP probe capabilities (especially fast MAS at low temperatures, LTMAS70), dedicated pulse sequences, new types of polarizing agents, and improved sample formulations yielding higher $\epsilon$ values and minimizing the intrusion of solvent signals. For example, ultra-LTMAS probes, using helium gas, have been shown to enable the achievement of $\epsilon$ values surpassing 600 with little or no relaxation penalty.68 The LTMAS probes capable of achieving spinning frequencies above 40 kHz will enable further improvements in sensitivity by the use of indirect detection. Pulsed schemes allowing a deeper penetration of hyperpolarized magnetization within microcrystalline compounds may greatly expand the scope of DNP. Notably, some of the most recent observations suggest that the Overhauser effect can become a useful mechanism for DNP, with great potential for applications at high magnetic fields. Similarly, very recently, a promising new class of biradical polarizing agents, known as TEMTriPols, yielded an unprecedented enhancement of $\epsilon$ = 65 at 800 MHz, which also extends efficient DNP to the ultrahigh field regime.71 On another front, it has been shown that large molecular weight nitroxide biradicals can offer respectable $\epsilon$ values (≥10) at a temperature of 200 K, suggesting that DNP measurements at even higher temperatures may very well be around the corner.53 The current pace of evolution in this field is tremendously fast such that recent breakthroughs in tools and methods rapidly become obsolete and at present the possibilities for new capabilities and impact to applications appear to be endless.

- REFERENCES