

3.4 Nuclear Magnetic Resonance (R. Mynott / C. Farès)

The NMR group provides a broad range of NMR techniques and analytical service to the entire institute. During the reporting period, approximately 35000 spectra have been recorded on a wide variety of samples ranging from organic and organometallic compounds in solution to coals and porous silicas in solids. To meet demands, the department is equipped with seven Bruker NMR spectrometers with field strengths corresponding to ^1H frequencies of 300 (x 2), 400 (x 2) and 600 MHz for analyses in solution and to 300 and 500 MHz for analyses in solid state. The department is also staffed with eight technical and scientific co-workers, skilled in NMR measurements and analyses as well as related soft- and hardware maintenance. The department is organized in four areas of service.

(1) NMR in Full Automation (R. Ettl / D. Bartels)

Basic NMR measurements in liquid state can be carried out in high throughput mode on two NMR spectrometers with ^1H frequencies of 400 and 300 MHz at room temperature. With minimal setup, scientific personnel from the institute can access these instruments round the clock and obtain NMR data which are acquired and processed fully automatically. The selection of available experiments is limited to those with high sensitivity, high information content and rapid execution with predefined parameters. These include experiments for 1D spectra of ^1H , ^{13}C , ^{31}P and ^{11}B as well as for 2D correlated NMR spectra such as $^1\text{H}/^1\text{H}$ COSY and $^1\text{H}/^{13}\text{C}$ HSQC. This service covers nearly 90% of all experiments run in our department.

(2) Routine NMR (R. Ettl / D. Bartels / W. Wisniewski / P. Philipps)

Liquid samples requiring special setup or treatment are submitted for measurement to our operators on two further 300 and 400 MHz spectrometers. The most common requests are for (a) experiments or nuclear frequencies not available in the automatic mode, (b) experiments at high or low temperature, (c) techniques requiring adjustment of acquisition parameters to optimize the spectra, and (d) spectroscopy of chemical reactions and kinetics followed in real time directly in the NMR tube.

(3) Advanced NMR Analyses (C. Wirtz / B. Gabor / P. Philipps)

Particularly challenging NMR studies of solution compounds are accepted for advanced analysis. For these samples, our technical staff members provide full measurement, analysis and interpretation assistance in close collaboration with the chemical research groups. The advanced techniques are carried out on our dedicated 600 and 400 MHz

NMR spectrometers. Since our last report, the 600 MHz spectrometer was implemented with a cryogenically cooled probehead, which considerably enhances signal-to-noise ratio up to a factor of 8 compared to conventional equipment. This important enhancement not only allows the full characterization of materials when the amounts are severely limited but also lowers the practical limits of powerful but less sensitive NMR experiments such as 2D-INADEQUATE. A large part of the analytical work is dedicated to determine or confirm structures, stereochemistries, conformations and dynamics. The most important spectroscopic projects are reported here:

- The NMR department has been closely involved in the spectroscopic assessment of the reaction steps leading to total syntheses of natural products from the Fürstner group. These included the berkelic acid, dictyodendrin alkaloids, the iejimalide-archazolid chimera, the lactimidomycin, the leiodolide B and the spirastrellolide F methyl ester. These studies entailed detailed structure and dynamics analyses which not only characterized the configuration of the products of every reaction step but also assisted in guiding the synthetic strategies.
- A number of organometallic complexes developed for catalysis were also characterized by advanced NMR. Strategies involving ^1H , ^{13}C , ^{31}P and ^{15}N nuclei allowed the identification of subtle chemical shift and coupling effects which helped to pinpoint the constitution of complexes involving gold, palladium, platinum and rhodium.
- NMR measurements over a temperature range were also used to characterize structural dynamics and reaction kinetics and mechanism. For instance, ^1H NMR was instrumental in unambiguously identifying carbenium cation species as the predominant reactive intermediates in gold-catalyzed rearrangement of cyclopropenone ketals.

(4) Solid-State NMR (B. Zibrowius / A. Ruffńska)

Solid-state NMR spectroscopy remains one of the most important techniques for the characterization of solid catalysts and other new materials synthesized in the institute. Both dedicated 300- and 500-MHz spectrometers are equipped with magic-angle spinning (MAS) probeheads to obtain high resolution signals from a wide range of NMR active nuclei. Specifically, the major fields of applications during the reporting period have been:

- Multinuclear (^{13}C , ^{29}Si , ^{31}P) MAS NMR investigations on the preparation of solid catalysts from mesoporous silicas (B. Zibrowius)
- Characterization of various complex aluminum hydrides and their (partially reversible) dehydrogenation by ^{27}Al NMR (B. Zibrowius)

- Characterization of doped sodium alanates applied as catalyst for partial hydrogenation of 1,3 butadiene by ^{27}Al , ^{23}Na and ^{13}C MAS NMR (B. Zibrowius)
- Mechanistic studies on the dehydrogenation process in sodium alanate by ^{27}Al and ^{23}Na MAS NMR (B. Zibrowius)
- Multinuclear (^1H , ^{13}C , ^{31}P) NMR investigations of structures, intra- and intermolecular dynamics and phase transitions of organometallic compounds at variable temperature (A. Ruffńska).
- Investigations of products obtained from the catalytic hydrogenation/hydrogenolysis of different types of coals (A. Ruffńska).

Methods Development (C. Wirtz)

With the hiring of a new group leader in 2010 (C. Farès) and the planned installation of a new 500 MHz instrument in 2011, the NMR department plans to develop new NMR methods applied to the field of chemical catalysis.

- Some preliminary work has been carried out to develop the use of residual dipolar couplings (RDC) for small chemical compounds. These parameters provide long-range information to complement the commonly-measured short-range NOE distance parameters. RDCs can determine stereochemistries, differentiate enantiomers and provide complementary conformational and dynamic information.
- The department has also begun the exploration of methods based on relaxation dispersion which permits the characterization of low-populated, high-energy intermediate states. Applied to transformation chemistry, this method can help identify the catalytically relevant transient intermediate and potentially help understand the important steps in reaction mechanisms.
- Finally, the tracking of catalytic transformation at atomic resolution in “real time” with rapid injection NMR technology is being prepared in order to identify short lived species and help reveal the progression of reactions.

Publications resulting from this area: 12, 164, 236, 258, 344, 404