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WORKSHOP ON
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CHARACTERIZATION OF SUPPORTED CATALYSTS BY SOLID STATE NMR

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I. Introduction: Some relevant spectroscopic considerations

Transient techniques, relaxation processes, dipolar interaction, chemical shift anisotropy, quadrupolar interaction, magic angle spinning, cross-polarization. 'Transient Techniques in NMR of Solids', by G. C. Gerstein and C. R. Dybowski.

II. Solid-state NMR of zeolites.

^{29}Si and ^{27}Al NMR, precursors in zeolite synthesis, composition of the aluminosilicate framework, Si-Al ordering, interaction with adsorbed species. J. M. Thomas and J. Klinowski, Adv. Catal., 33, 199 (1985).

III. Structure of aluminas. C. S. John et al. Applied Catal., 6, 341 (1983).

IV. Characterization of silica-alumina gels.

Homogeneity of Si-Al interaction in cracking catalysts, effect of silica on alumina porosity and acidity.

V. Surface phases of Ni-Mo/Al_2O_3 hydrodesulfurization catalysts.

^{95}Mo, ^{27}Al and ^{31}P NMR, deactivating surface phases. M. McMillan et al. J. Catal., 97 243 (1986).

VI. CO, H_2 and hydrocarbon adsorption on supported metal particles.

^{195}Pt and ^{13}C NMR, bonding of CO to group VIII metals, structure of adsorbed C_2 hydrocarbons, observation of chemical reaction and reaction products. C. P. Slichter, Ann. Rev. Phys. Chem., 37, 25 (1986).

Spectroscopies for

Structural Characterization of Catalysts

- Mössbauer — Fe, Co, Sn; Ru, Pt, Au
- NMR
- EXAFS

All are: Element specific,

sensitive to local environment, and

do not require long-range order,

but all are bulk techniques also.

Selected References

General principles

C. P. Slichter, "Principles of Magnetic Resonance", 2nd ed., Springer-Verlag, Heidelberg, 1978.

NMR of Solids

Theory - H. C. Torrey and C. R. Dybowski, "Transient Techniques in NMR of Solids", Academic Press, 1985.

Applications - C. A. Fyfe, "Solid State NMR for Chemists" C.F.C. Press, Guelph, Ontario, Canada, 1983.

Catalytic Applications

Chemisorption — T. M. Duncan and C. Dybowski, Surf. Sci. Rep. 1, 157 (1981).

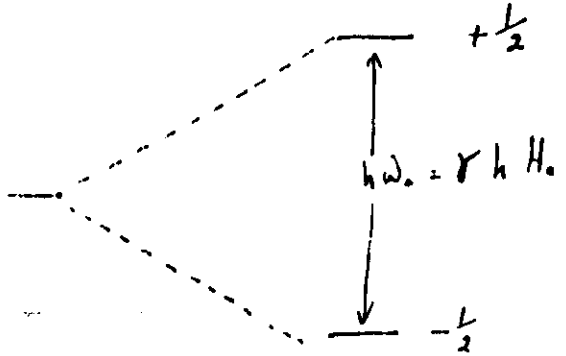
Zeolites and Silica-Alumina — J. M. Thomas and J. Klinowski, Adv. Catal., 33, 199 (1985).

Supported Metals — C. P. Slichter, Ann. Rev. Phys. Chem., 37, 25 (1986).

Principal Magnetic Interactions

Interaction	Approximate Range (Hz)	
Zeeman	$10^6 - 10^9$	H_0 dependent
Dipolar	$0 - 10^5$	
Chemical Shift	$0 - 10^5$	H_0 dependent
Spin-Spin Coupling	$0 - 10^4$	
Quadrupolar	$0 - 10^9$	(Invariant H_0 dependent to second-order)

Zeeman Interaction for $I = \frac{1}{2}$, e.g., ^{13}C

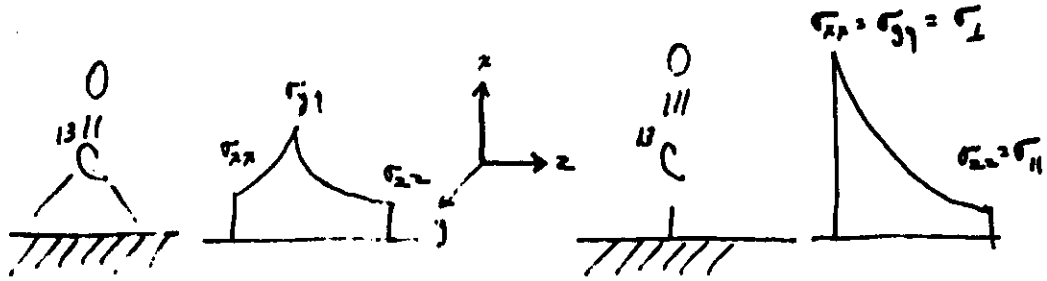


Increasing Applied Magnetic Field, H_0

Field and Spin Interactions are Three Dimensional

Interaction	Tensor	Motional Average
Dipolar	$\hat{D}$	0
Chemical Shift	$\hat{\sigma}$	$\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$
Spin-Spin Coupling	$\hat{J}$	$\frac{1}{3}(J_{xx} + J_{yy} + J_{zz})$
Quadrupolar	$\hat{eq}$	0

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \xrightarrow[\text{(choice of an appropriate coordinate system}]{\text{diagonalization}} \begin{bmatrix} \sigma_{xx} & & \\ & \sigma_{yy} & \\ & & \sigma_{zz} \end{bmatrix}$$



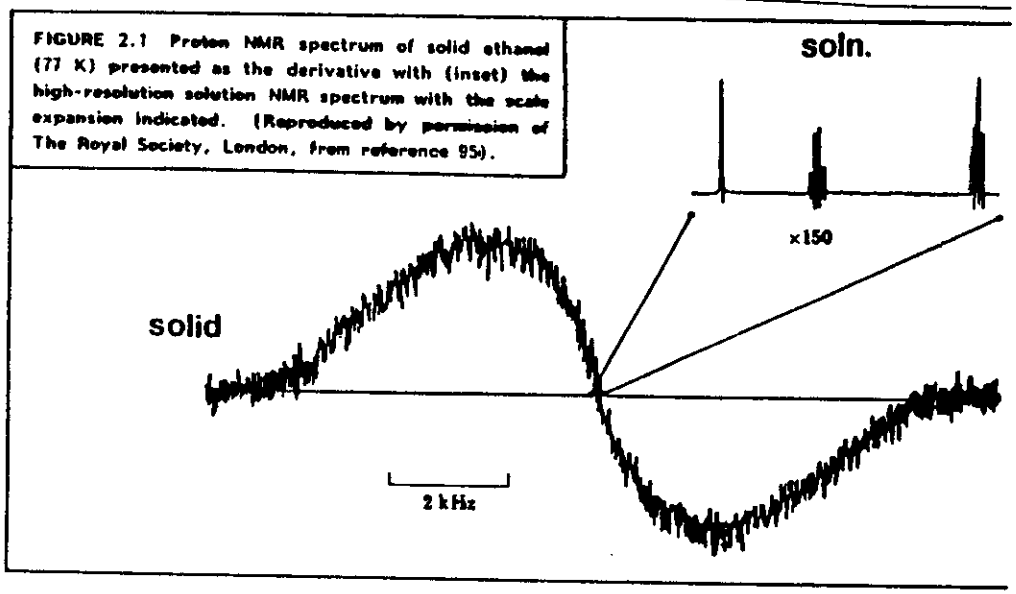


FIGURE 2.1 Proton NMR spectrum of solid ethanol (77 K) presented as the derivative with (inset) the high-resolution solution NMR spectrum with the scale expansion indicated. (Reproduced by permission of The Royal Society, London, from reference 95).

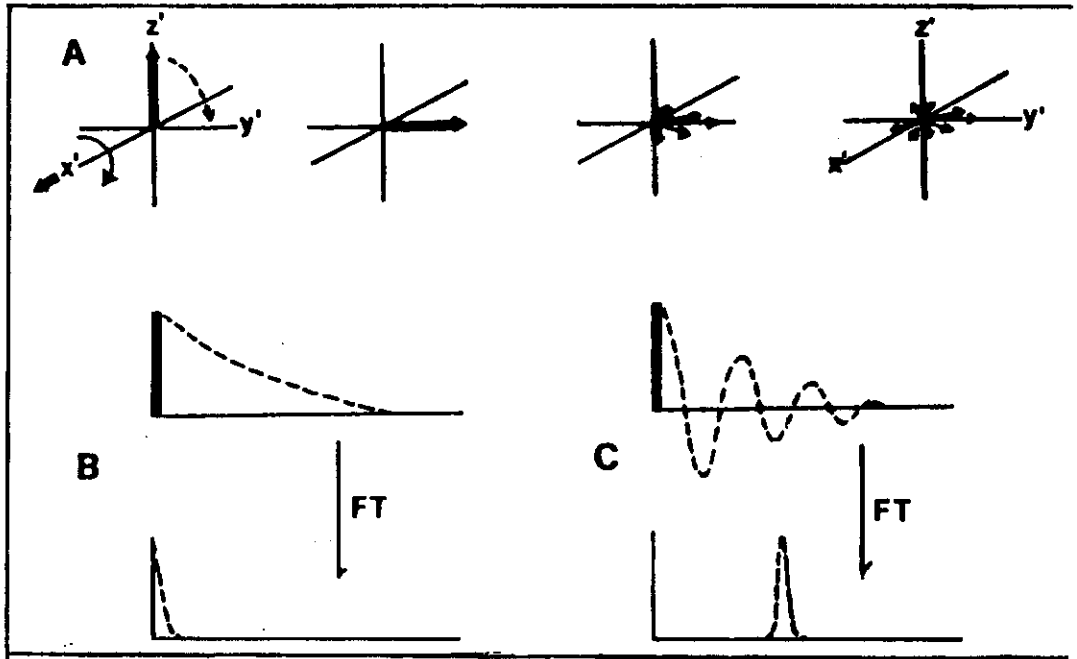
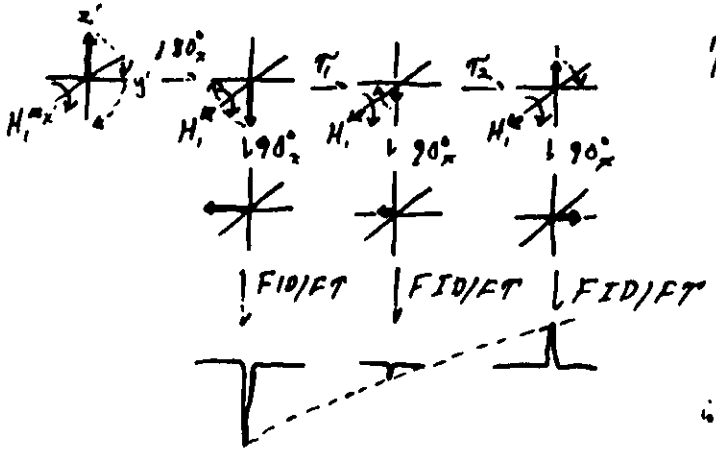


FIGURE 2.17 Schematic representation of the pulse-F/T sequence in the rotating frame of reference showing (A) the behaviour of the magnetization as a function of time after being rotated 90° by an on-resonance RF pulse applied along the x' axis and the subsequent dephasing of the spins in the x'y' plane and (B) and (C) the magnetization decay and its Fourier transform detection exactly on resonance and slightly off resonance respectively.

Special problems with solids:

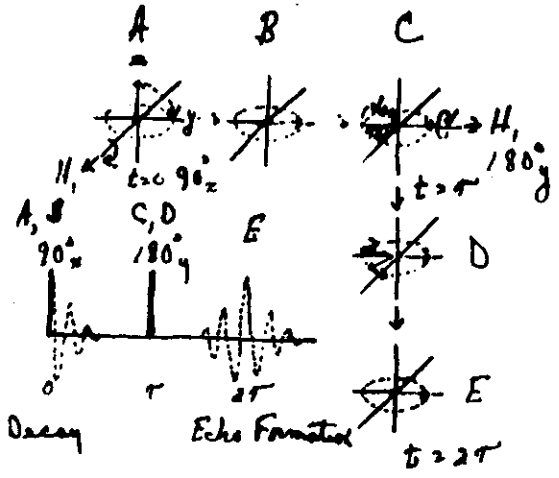
1. Receiver "dead-time"
2. High power pulses
3. Fast digitizer to cover total frequency width

Relaxation Time Measurement



T_1, spin Lattice relaxation time (longitudinal relaxation time)

For a solid, T_1 is long, e.g. tens of seconds to hours.



T_2, spin-spin relaxation time (transverse relaxation time)

Line width $\propto (\pi T_2)^{-1}$

For solids, T_2 - short, e.g., microseconds.

Magic Angle Spinning (MAS) NMR

Magic angle - $54^\circ\ 44'\ 8''$

$(3\cos^2\theta - 1) \rightarrow 0$

MAS Removes:

Dipolar coupling

Chemical shift anisotropy

First order quadrupolar effects

Topics to be Discussed

Silica Modification of Alumina Supports

^{29}Si, $I=\frac{1}{2}$, 4.7% NA, 99.33 MHz, 11.74 T

Surface Structures of Calcined Hydrodesulfurization Catalysts

^{27}Al, $I=\frac{5}{2}$, 100% NA, 130.29 MHz, 11.74 T

^{31}P, $I=\frac{1}{2}$, 100% NA, 202.41 MHz, 11.74 T

^{95}Mo, $I=\frac{5}{2}$ 15.72% NA, 32.57 MHz, 11.74 T

Bonding of CO and C_2H_4 to Pt and Pd

^{13}C, $I=\frac{1}{2}$ 1.108% NA, 25.144 MHz, 2.35 T

75.144 MHz, 7.05 T

Conclusions

1. Analysis of structure of silica-alumina with SiO_2 conc. as low as 1 wt% are practical.
2. All preparations, including co-precipitation, result in rather heterogeneous mixtures.
3. Post precipitation impregnation of alumina gel by Na silicate solution results in surface orthosilicate and (cyclic) metasilicate almost exclusively.
4. A high metasilicate/orthosilicate ratio correlates with increased thermal stability of the alumina support.
5. Acid sites, as measured by cumene cracking, correlates with total silica and not a particular structure measured by NMR.

Conclusions

1. MAS-NMR can be used to detect (well ordered) surface phases of elements where most of the element is in the bulk, e.g. ^{27}Al in Al_2O_3.

2. Well ordered domains of MoO_3 are formed in MoO_3/Al_2O_3 but not in $NiMoP/Al_2O_3$.

3. In an industrial $NiP\,Mo/Al_2O_3$, surface phases of $AlPO_4$ form below 700°C and $Al_2(MoO_4)_3$ forms between 700 - 800°C.

4. Surfaces phases of $Ni_2(MoO_4)_3$ form at lower temperature in MoO_3/Al_2O_3 than in $NiMoP/Al_2O_3$. P may play a role in inhibition of MoO_3-Al_2O_3 reaction.