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Preface

For more than five decades, the methods of surface physics and chemistry have provided some of the most incisive results advancing our understanding of the catalytic action of solids at the molecular scale. Characterizations by physical methods have demonstrated the dynamic nature of catalyst surfaces, showing that their structures, compositions, and reactivities may all be sensitive to temperature and the composition of the reactive environment. Thus, the most insightful catalyst characterizations are those of catalysts as they function. This volume of *Advances in Catalysis* is dedicated to the topic of physical characterization of solid catalysts in the functioning state. Because the literature of this topic has become so extensive, the representation will extend beyond the present volume to the subsequent two volumes of the *Advances*.

The literature of this subject has generated its share of jargon, which has been held to a minimum in the following contributions. The term *in-situ* is widely used to describe catalyst characterization experiments, but with inconsistent meanings. We suggest that it might be best to use this term to describe experiments with strict control of all parameters that might affect the surface properties of a catalyst, whether or not a catalytic reaction may be operative. We have preferred to minimize use of this term and to refer explicitly to functioning, working, or operating catalysts when appropriate. Alternatively, the term *operando* has been applied (e.g., B. M. Weckhuysen, *Phys. Chem. Chem. Phys.* **5**, 4351 (2003)) to the characterization of catalysts by spectroscopic methods with simultaneous measurements of catalytic activity (and/or selectivity and/or stability). Unfortunately, many authors have used this term more loosely, for example, without reporting any catalyst performance data, and it seems to be at risk of becoming as vague in usage as "in situ;" we largely avoid it in this set of volumes.

It is generally desirable to integrate measurements representing a working catalyst surface with measurements that characterize the activity, selectivity, and/or stability of the catalyst, such as can be determined by use of gas chromatography or mass spectrometry of products. It is important to keep in mind that when a reactor is designed to serve optimally as a cell for measurements of catalyst surface properties, it may not be the kind of ideal reactor that would provide activity, selectivity, or stability data that can be interpreted fundamentally in terms of kinetics and chemical reaction engineering.

The growing interest in physical characterization of solid catalysts as they function has stimulated a new series of congresses, the first held in Lunteren (The Netherlands) in 2003 and the second in Toledo in 2006. The subject has been documented in recent books (B. M. Weckhuysen, Ed., "In situ Spectroscopy of Catalysts," American Scientific Publishers, 2004, and J. F. Haw, Ed., "In situ Spectroscopy in Heterogeneous Catalysis," Wiley-VCH, 2002) and in topical issues of journals: *Top. Catal.* **15** (2001); *Phys. Chem. Chem. Phys.* **5**, issue 20 (2003); and *Catal. Today* **113** (2006). It is our intention that our set of volumes be more nearly comprehensive than these publications, as well as providing many newer results.

In the present volume, Gladden, Mantle, and Sederman summarize the application of magnetic resonance imaging techniques to represent both local flow fields in reactors containing solid catalyst particles and conversions within model reactors. The techniques provide a non-invasive, chemically specific measurement technique that leads to representation of a reactor over length scales ranging from Angstroms to centimeters.

Hansen, Helveg, and Datye report on atomic-scale imaging of supported metal nanocluster catalysts in the working state. High-resolution transmission electron microscopy allows atomic-resolution imaging of transition metal catalysts during exposure to reactive gases at elevated temperatures, providing insights into the structure, morphology, and dynamics of supported catalysts with various surfaces and interfaces as they function. Examples include evidence of the location of a barium promoter in a ruthenium catalyst for ammonia synthesis and environment-induced morphology changes in supported copper catalysts for methanol synthesis.

Lauritsen and Besenbacher summarize research on model catalyst surfaces investigated by scanning tunneling microscopy (STM). They show atomic-scale information obtained by STM elucidating the formation of surface alloys; wetting; blocking of reactive step edges; and identification of electronic states at the edges of nanoclusters. These results have helped to guide the preparation of new high-surface-area catalysts.

Hunger and Wang provide an account of advances in the characterization of solid catalysts in the functioning state by nuclear magnetic resonance spectroscopy. Examples include investigations of zeolite-catalyzed reactions with isotopic labels that allow characterization of transition states and reaction pathways as well as characterization of organic deposits, surface complexes, and reaction intermediates formed in catalyst pores.

Bürgi and Baiker summarize progress in the application of attenuated total reflection infrared spectroscopy for investigation of solid catalysts functioning in the presence of liquid-phase reactants. The technique allows the detection of liquid-phase products and the investigation of species adsorbed on catalysts during reaction, even in the presence of strongly adsorbing solvents. Under some conditions, changing catalyst structures can be investigated with this technique.

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Magnetic Resonance Imaging of Catalysts and Catalytic Processes

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Magnetic resonance (MR), in the form of solid-state nuclear magnetic resonance (NMR) spectroscopy, is well established as a research tool for investigations of the structures of solid catalysts and molecular species adsorbed on them. However, during the past decade there has been increasing interest in using magnetic resonance imaging (MRI) techniques to study, in particular, flow fields inside reactors. These studies have recently been extended to measurements of chemical conversion within model reactor systems. The real power of MR techniques is that by bringing together spectroscopy, diffusion, micro-imaging, and flow imaging, they provide a non-invasive, chemically specific measurement technique which can characterize a system over length scales ranging from the angstrom- to the centimeter scale. In this review, recent developments in MRI pulse sequences are summarized and applications to investigations of both hydrodynamics and catalytic conversion within catalysts and catalytic reactors are presented.

Materials: 2M2B; 2-methyl-2-butene; HZSM-5; zeolite with MFI framework (IUPAC nomenclature); NaCaA; zeolite with LTA framework (IUPAC nomenclature); NaX; zeolites with FAU framework (IUPAC nomenclature); Pd/Al_2O_3; alumina supported palladium catalyst; TAME; tert-amyl methyl ether or 2-methoxy-2-methylbutane; TAOH; tert-amyl alcohol or 2-methyl-butan-2-ol

Abbreviations: BET; Brunauer Emmett Teller; adsorption isotherm model; BLIPPED EPI; MR pulse sequence; CFD; computational fluid dynamics; CSI; chemical shift imaging; MR pulse sequence; DANTE; delays alternating with nutations for tailored excitation; MR pulse sequence; DANTE TOF; delays alternating with nutations for tailored excitation time of flight; MR pulse sequence; DEPT; distortionless enhancement by polarization transfer; MR pulse sequence; EPI; echo planar imaging; MR pulse sequence; FID; free induction decay; FLASH; fast low-angle shot; MR pulse sequence; FSE; fast spin echo; MR pulse sequence; GERVAIS; gradient echo rapid velocity and acceleration imaging sequence; MR pulse sequence derived from EPI; GRASE; gradient and spin echo; MR pulse sequence; MBEST-EPI; modulus blipped echo planar single-pulse technique; MR pulse sequence derived from EPI; MR; magnetic resonance; MRI; magnetic resonance imaging; NMR; nuclear magnetic resonance; Pe; dimensionless group characterizing flow; PEPI, π-EPI; MR pulse sequence derived from EPI; PFG; pulsed field gradient; MR pulse sequence; PGSE; pulsed gradient spin echo; MR pulse sequence; RARE; rapid acquisition with relaxation enhancement; MR pulse sequence; Re; Reynolds number; dimensionless group characterizing flow; REPI; radial EPI; MR pulse sequence derived from EPI; SEMI-RARE; single excitation multiple image rapid acquisition with relaxation enhancement; MR pulse sequence derived from RARE; SNAPSHOT; MR pulse sequence; SPRITE; single point ramped imaging with T_1 enhancement; MR pulse sequence; TMS; tetramethylsilane; TOF; time of flight; TSE; turbo spin echo; MR pulse sequence

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Nomenclature: *Greek*, Δ; observation time in transport measurement pulse sequence (s), Φ; net phase offset (rad), γ; gyromagnetic ratio ($\mathrm{rad\,s^{-1}\,T^{-1}}$), δ; time for which pulsed magnetic field gradient is applied (s), ϕ; phase offset (rad), χ; liquid holdup, χ_{dynamic}; dynamic liquid holdup, χ_{s}; surface wetting, θ; pulse angle (rad), ρ; spin density ($\mathrm{m^{-3}}$), τ; delay time (s), ω; angular frequency ($\mathrm{rad\,s^{-1}}$), ω_0; resonance or Larmor frequency ($\mathrm{rad\,s^{-1}}$): *Roman*, B; magnetic field (T), B_0; external magnetic field (T), G; magnetic field gradient for imaging ($\mathrm{T\,m^{-1}}$), M; magnetization ($\mathrm{A\,m^{-1}}$), M_0; equilibrium magnetization ($\mathrm{A\,m^{-1}}$), P_{s}; displacement propagator, S; acquired signal intensity, T_1; spin–lattice relaxation time (s), T_2; spin–spin relaxation time (s), T_2^*; time constant of the free induction decay in the presence of B_0 inhomogeneities (s), X; conversion, a; acceleration ($\mathrm{m\,s^{-2}}$), e; component of the stress tensor ($\mathrm{s^{-1}}$), g; magnetic field gradient employed in transport measurements ($\mathrm{T\,m^{-1}}$), $\mathbf{k}$; reciprocal space vector employed in imaging ($\mathrm{m^{-1}}$), $\mathbf{q}$; reciprocal space vector employed in transport measurements ($\mathrm{m^{-1}}$), $\mathbf{r}$; position vector (m), t; time (s), t_{d}; delay time in the spin–echo pulse sequence (s), v; velocity ($\mathrm{m\,s^{-1}}$), x, y, z; Cartesian laboratory-frame coordinates, x', y', z'; Cartesian rotating-frame coordinates

I. Introduction

Until the early 1990s, application of magnetic resonance (MR) to studies of *in situ* catalysis was almost exclusively the domain of the chemist employing increasingly sophisticated solid-state MR pulse sequences to investigate the mechanisms of catalytic processes. Such work has been reviewed extensively by many workers, including Packer (*1*), Dybowski *et al.* (*2*), Roe *et al.* (*3*), Baba and Ono (*4*), Fraissard (*5*), Haw (*6*), Ivanova (*7*), Parker (*8*), van der Klink (*9*), Hunger and Weitkamp (*10*), and Han *et al.* (*11*). These reports of *in situ* catalysis address the molecular-scale events occurring during the catalytic process and give valuable information regarding structure–function relationships in catalytic materials. To a lesser extent, spatially unresolved measurements of molecular diffusion have been made within catalysts by use of pulsed field gradient (PFG) techniques (e.g., Kärger and Freude (*12*)). The present review is an evaluation of the role of MR in investigations of *in situ* catalysis from a quite different perspective—that of imaging.

Traditionally the technique of the medical physicist, magnetic resonance imaging (MRI) has long been used to investigate the internal structure of the human body and the transport processes occurring within it; for example, MRI has been used to characterize drug transport within damaged tissue and blood flow within the circulatory system. It is therefore a natural extension of medical MRI to implement these techniques to study flow phenomena and chemical transformations within catalysts and catalytic reactors.

Figure 1 is a schematic illustration of the length scales probed by various MR techniques and the areas of catalysis that can therefore be addressed. Across these length scales, the ability of MR to quantify both structure and dynamics, non-invasively and with chemical specificity within optically opaque systems, offers great opportunities for increasing our understanding of catalysts and catalytic reactors. Existing MRI investigations tend to fall into two broad categories:

Microimaging studies of single catalyst pellets. In these investigations, spatial resolutions of ~30–50 μm are typically achieved, and steady- and unsteady-state

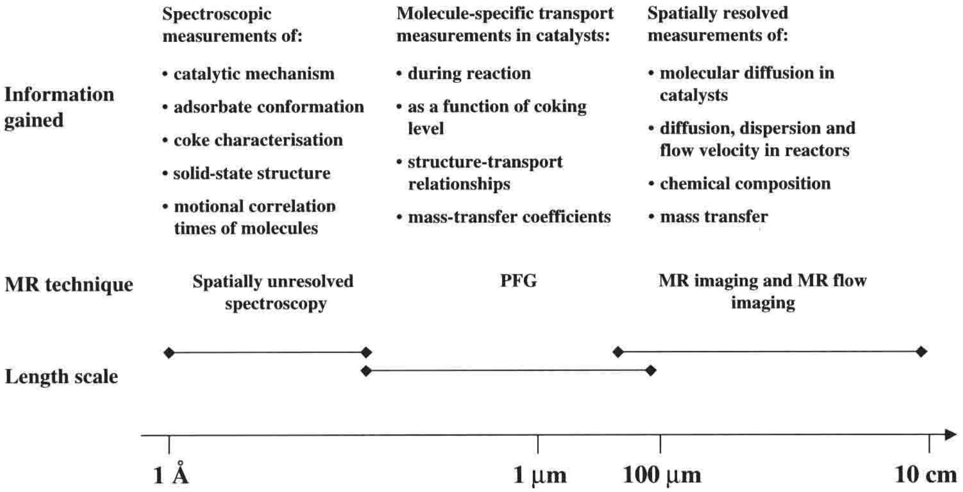

FIG. 1. The MR Toolkit: MR techniques yield information about chemical and physical processes over length scales of Å to cm. Imaging pulse sequences may be integrated with spectroscopy and molecular diffusion measurements providing maps of chemical composition and molecular transport phenomena at spatial resolutions of 30–500 μm.

liquid distributions within the individual pellets have been imaged. A variety of applications has been reported. For example, the characterization of processing–structure–function relationships in catalyst manufacture and, in particular, the effect of catalyst manufacturing processes on the micro- and meso-scale pore structure of the resulting catalyst pellet and hence the molecular transport processes occurring within the catalyst. The same methods also lend themselves to investigation of liquid transport processes during catalyst preparation, such as liquid and ion transport occurring during a catalyst preparation by ion exchange. With respect to the catalytic reaction process itself, liquid re-distribution as a result of temperature gradients caused by chemical reaction has been demonstrated. Coke deposition can also be followed.

Microimaging and flow imaging of reactors. MRI has found considerable success in imaging the internal phase distributions and liquid flow fields inside reactors, at spatial resolutions of 100–500 μm. The dimensions of systems studied are constrained to the dimensions of the bore of the superconducting magnet used. In vertical bore systems, standard magnet hardware allows reactor diameters of 2.5–6 cm to be investigated, with a similar field-of-view along the direction of the axis of the magnet. In the case of horizontal bore systems, medical imaging magnet technology provides magnet bores of ~30 cm in diameter, which provide a field-of-view of ~20 cm in vertical and horizontal directions. Although these constraints do not allow us to study the large fixed-bed catalytic processes used in plants in, say, the petroleum refining sector, we are able to investigate scaled-down reactors of dimensions typical of those used in industrial research and development. Furthermore, with increasing interest in the design of micro-reactor technologies, many new reactor designs do actually fit inside the magnet at full scale.

The motivation to extend these measurements and, in particular, to integrate MR spectroscopy, transport measurements, and imaging techniques is strong. In principle, we should be able to study the behavior of a single catalyst pellet within a reactor while it is operating within the fixed bed and observe directly the effects of catalyst form (i.e., pellet size and shape) and reactant–solid contacting patterns within the reactor on overall catalyst activity, selectivity, and lifetime. MR offers the opportunity to bridge the length scales from the angstrom- to the centimeter scale by incorporating MR spectroscopy into imaging strategies, thereby spatially resolving spectral acquisition. Currently, such imaging experiments are in their infancy and yield spatial resolutions of the order of 50–600 μm, sufficient to show, for example, the spatial variation of conversion within a fixed-bed reactor. To use MR routinely in *in situ* studies of catalysis, new MR techniques will have to be developed and implemented to retain the inherent, quantitative nature of the MR measurement in catalyst and reactor systems, which are characterized by strong variations in magnetic susceptibility and fast nuclear spin relaxation time processes. In this regard, catalyst and reactor systems are very different from the human body in terms of the sample response to the radio frequency excitation and pulsed magnetic field gradients used in an MR experiment; consequently, medical MRI strategies do not translate directly into catalysis research. It is also worth reiterating the known limitations of MR techniques regarding systems that can be investigated. From a practical point of view, large ferromagnetic objects cannot be handled within and close to a superconducting magnet. However, units comprising aluminum and brass can be used within the magnet. With respect to the sample itself, the ability to characterize a given system is very material-specific. Ferromagnetic and paramagnetic particles act to distort the local magnetic fields and influence relaxation times within the sample, thereby making all investigations based upon quantitative analysis extremely challenging. However, each system should be considered on a case-by-case basis. For example, the strong influence of paramagnetic ions on signal intensity can be successfully exploited to follow the evolution of redox reactions with time.

The aim of this review is to introduce the language of MRI to the catalysis community and to describe the early achievements in this field. The structure of this article is as follows:

(a) Section II introduces the principles of MRI methods and describes the MRI pulse sequences currently used in *in situ* studies of chemical reactors.
(b) Sections III and IV review work done in imaging fluid distribution and transport at the length scale of catalyst pellet (Section III) and reactor (Section IV).
(c) Section V brings together the work done in spatially resolving spectroscopic measurements within model reactor environments; these experiments allow us to follow reactions *in situ*.
(d) Section VI provides a brief forward look on the future role of MRI in catalysis research.