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1O2 with bulk Al (3f) and with the Al13− cluster. Because the interpretation of the low bulk reactivity remains unsettled, the results presented here may prove useful in unraveling the controversy surrounding the interpretation of solid-state aluminum reactivity. Furthermore, spin states play an important role in long-known oxidation processes (e.g., O2:NO/NO2, O2:SO2/SO3), and also in the oxidation of carbon compounds: The first detailed experimental and theoretical data for 1O2 reactions with 2 + 4 and 2 + 2 cycloadditions were presented only a decade ago (28). Thus, the present results may initiate further FT-ICR investigations of 1O2 and 3O2 reactions in many other chemical oxidation processes that affect our daily lives, e.g., in biology (respiration), engineering (corrosion), and energetics (combustion).

References and Notes

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Catalysis is vital to industrial chemistry, and the optimization of catalytic reactors attracts considerable resources. It has proven challenging to correlate the active regions in heterogeneous catalysts with morphology and to monitor multistep reactions within the bed. We demonstrate techniques, using magnetic resonance imaging and para-hydrogen (p-H2) polarization, that allow direct visualization of gas-phase flow and the density of active catalyst in a packed-bed microreactor, as well as control over the dynamics of the polarized state in space and time to facilitate the study of subsequent reactions. These procedures are suitable for characterizing reactors and reactions in microfluidic devices where low sensitivity of conventional magnetic resonance would otherwise be the limiting factor.

Catalysis is a fundamental component to many industrial processes and, consequently, the optimization of catalytic reactions and reactors attracts considerable technological effort and financial commitments. An important aspect of this optimization is to correlate the spatial distribution of the reactive conversion inside the reactor with the morphology and packing of the catalyst. Here, we describe a spectroscopic method for this purpose based on magnetic resonance imaging (MRI) (1) that uses hyperpolarized spins derived from p-H2 (2, 3). Specifically, we achieve high-resolution, spatially resolved profiles of heterogeneous hydrogenation reactions taking place at a solid-gas interface inside a microreactor. We demonstrate strongly enhanced nuclear magnetic resonance (NMR) signal intensities in the gas phase as well as precise control over the spatiotemporal dynamics of the polarization. The enhanced sensitivity is particularly important for tracking gases and products in small volumes (e.g., in microfluidic devices (4, 5) or the limited void space of a tightly packed catalyst bed). Moreover, the controlled delivery of p-H2–induced nuclear spin polarization acts as a spin label that can transport polarization to remote regions in the reactor. This work has implications for studying kinetics and mechanisms of multistep heterogeneously catalyzed reactions and fluid-flow transport, as well as mass and heat transfer. Such characterization should facilitate improved reactor and catalyst design.

Methods to optimize microreactors would be welcome in the context of microfluidic (lab-on-a-chip) technology. In recent years, the compelling advantages of microfluidic technology (4, 5) in biopharmaceutical applications, chemical analysis (6), organic synthesis (7, 8), and industrial catalysis have been recognized and demonstrated

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Various techniques have been used to study the motion of fluids in catalytic processes. For example, capacitance (16), single-photon emission–computed tomography (17), and positron emission tomography (18) are used to monitor gas-liquid distributions in multiphase reactors. But these methods measure average flow properties and have limited spatial resolution. The use of MRI to characterize microreactors is advantageous because the technique is noninvasive, can probe optically opaque media, and is appealing for catalysts because of the variety of molecular parameters that can be mapped with considerable chemical and spatial selectivity (19). Specifically, flow maps and local density profiles can be generated, molecular mobility can be tracked, and chemical reaction mechanisms can be probed with spin-labeled nuclei (20). Previous applications of MRI to heterogeneous catalysis included studies of hydrogenation processes without $p$-$\text{H}_2$ (21, 22), catalyst morphologies and synthesis techniques (23, 24), and fluid flow through the catalyst bed (25), as well as monitoring of esterification reactions (12, 13) in situ. All of these applications were based on the NMR signal detection of the liquid phase and thus offer a sensitivity that is three orders of magnitude larger as compared with gases, resulting from the difference in density. The sensitivity enhancement offered by $p$-$\text{H}_2$–induced polarization (PHIP) is essential for the application of MRI to heterogeneous chemical reactions in the gas phase.

$p$-$\text{H}_2$ (2, 3, 26) is characterized by a singlet nuclear spin wave function and is relatively easy to prepare in quantum-state ensembles of very high purity. The total nuclear spin angular momentum of this state is zero, resulting in no observable NMR signal. However, if the protons participate in pairwise hydrogenation in which they become magnetically inequivalent, strong observable magnetization can be produced (2, 3, 26) with a signal enhancement factor typically on the order of 10^4.

For instance, if $p$-$\text{H}_2$ is used in the hydrogenation of propylene into propane (27, 28), the $p$-$\text{H}_2$–derived protons will be in the singlet state immediately after the transformation of the substrate molecule into the product molecule. Typically, the molecular additions occur at randomly distributed times, and the result is an incoherent but highly polarized nuclear spin state. Application of suitable radio-frequency (rf) pulses results in a hyperpolarized NMR signal (29). However, if an isotropic mixing sequence is applied during the course of the reaction, not only is a coherent singlet state preserved, but the lifetime of this state is also increased (30). As we demonstrate below, this effect allows one to create a relatively long-lived, coherent packet of polarized product molecules, which augments the versatility of this technique beyond hydrogenation reactions.

To demonstrate the effectiveness of heterogeneously catalyzed PHIP in microreactors, we use two model catalytic reactors (29) (Fig. 1). In both cases, propylene and $p$-$\text{H}_2$ gases are flowed through the catalyst bed and react to form propane. The first reactor (reactor 1) contains a tightly packed bed of the silica gel–immobilized Wilkinson's catalyst located between two layers of glass beads. This reactor is used to produce a highly polarized product (propane) and illustrates the ability to resolve flow maps, active regions in the catalyst bed, and controlled transport of polarization out of the catalyst bed. The second reactor (reactor 2) comprises powdered Wilkinson's catalyst loosely packed with some small (~2-mm) air gaps. This second reactor further demonstrates the control of a polarized outstream and applications to a more heterogeneous packing.

The PHIP signal in these experiments is larger than the corresponding thermal signal by a factor of 300 (29). This enhancement is crucial in light of the coil-sample arrangement. The ratio of the rf coil volume occupied by the microchannel to the rf coil volume is less than 0.01: a situation that is unfavorable in terms of detection
sensitivity. Furthermore, the presence of catalyst powder occludes the space inside the microchannel. This sensitivity loss, combined with the low density of the gas, leads to a million-fold loss in sensitivity relative to standard liquid-state NMR. Our experimental results show that PHIP can, to a large extent, circumvent the problem of low sensitivities in gas-phase microreactors.

An image of the first reactor is shown in Fig. 2. The spatial distribution of reactant (propylene) is barely resolved (Fig. 2A), whereas the polarized product (propane) shows a strongly enhanced signal (Fig. 2B). We also compare a spectrum from the reactor (fig. S2A) and localized spectra from upstream of (fig. S2B) and in (fig. S2C) the catalyst bed. The use of a hyperpolarized substance was also necessary for producing the high-resolution gas-phase flow map shown in Fig. 2C (29). This example reveals heterogeneous flow patterns in the catalyst bed, which are consistent with a non-uniform packing of the catalyst (29), that are not apparent in Fig. 2B. Flow imaging at the same resolution and sensitivity would not be possible with the exceedingly weak thermal signals.

As illustrated in Fig. 3A, the residence time inside the tightly packed region leads to nearly complete magnetic relaxation, and no polarized product is observed beyond the catalyst bed. Although this outcome is ideal for imaging the active regions of the catalyst bed, the polarized spins cannot be used for subsequent reactions. Isotropic mixing sequences have been shown to prolong the lifetime of the nuclear spin-singlet state (30). Thus, the use of an isotropic mixing sequence (31) applied for a sufficiently long duration $T_m$ allows the polarized product to escape the catalyst bed (the optimal $T_m$ will depend on the average flow velocity $v$). This period is followed by a delay $T_d$, allowing the singlet state to travel a distance $x = v \times T_d$ during which the singlet state evolves into a state observable by NMR. By varying $T_d$, we control the distance traveled before the polarization is released. Figure 3, B and C, demonstrates the delivery of polarized product beyond the catalyst bed for two values of $T_d$.

Imaging of the second reactor (Fig. 4A) further demonstrates the usefulness of controlling the polarized outstream. In contrast with the packing in reactor 1, the looser packing in reactor 2 results in a polarized product that can be seen escaping the first catalyst layer and flowing to the second layer in the absence of singlet state preservation ($T_m = 0$ ms, $T_d = 0$ ms). Although this situation is desirable when the polarized product is to be used in subsequent reactions, it is problematic as a means for imaging the catalyst layer because of poor contrast and blurring from the uncontrolled flow of polarized product. This drawback can be remedied by controlling the singlet state as follows. For short values of $T_d$ (1 ms), no polarized product can be seen between the catalyst layers, because the singlet state has not yet evolved into an observable state. At longer time intervals ($T_d = 100$ ms), the polarized product has traversed longer distances and evolved into an observable polarized product. A photograph of the reactor (Fig. 4B) provides a comparison of the distribution of catalyst in the reactor with the structural morphology observed in the MRI images.

Regardless of the packing, singlet state preservation provides a distinctive method for controlled delivery of polarization. Combined with knowledge of the local flow velocity, the timed release of polarization can be performed in remote parts of a microreactor. Thus, in multistep reactions, the polarized product can be used as a spin label to elucidate subsequent stages of a reaction (20).

These experiments can be extended by means of a variety of polarization transfer and spin manipulation methods to move the enhanced signal to other NMR-active nuclei on the substrate molecule or onto the catalyst itself (14, 20). Transfer of polarization to heteronuclei yields a larger range of chemical shifts as compared with that of protons (14). The highly polarized spin product also makes it possible to image flows (32) and reactions (33) in precisely engineered microchannels noninvasively, opening the way for a variety of microfluidic applications.

There are still many challenges to address before these results can be extended to a wider range of hydrogenation reactions and conditions of industrial catalytic processes. In particular, it remains to be seen to what extent the polarization lifetimes and the NMR linewidths of the reaction products are affected by the presence of metal catalyst surfaces, microscopic gradients of magnetic susceptibility, high temperatures, paramagnetic catalysts and impurities, liquid films, and other complications that can be expected under conditions encountered in practice. To this end, recent results (34) that demonstrate PHIP in heterogeneous hydrogenations catalyzed by supported metal catalysts (Pt/Al2O3 and Pd/Al2O3) are encouraging.

References and Notes

GaN Photonic-Crystal Surface-Emitting Laser at Blue-Violet Wavelengths

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Shorter-wavelength surface-emitting laser sources are important for a variety of fields, including photonics, information processing, and biology. We report on the creation of a current-driven blue-violet surface-emitting laser. This represents an important step in the development of laser sources that could be focused to a size much less than blue-violet wavelengths by the use of optical tweezers for ultrafine manipulation.

The lasing principle of photonic-crystal surface-emitting lasers (PC-SELS) (1-5) is based on the band-edge effect in a two-dimensional (2D) PC, where the group velocity of light becomes zero and a 2D cavity mode is formed. The output power is coupled to the vertical direction by the PC itself, which gives rise to the surface-emitting function. PC-SELS have the following features: first, perfect, single longitudinal and lateral mode oscillation can be achieved even when the lasing area becomes very large (for example, devices >300 µm in diameter) (1, 3, 5); second, the polarization mode (3) and the beam pattern (5) can be controlled by appropriate design of the unit cell and/or lattice phase in the 2D PC. However, the shortest lasing wavelength achieved so far is 980 nm. A lasing wavelength in the blue-to-ultraviolet region would open the door to a much broader range of applications such as super-high-resolution laser sources, which can be focused to spot sizes smaller than blue-violet wavelengths by the use of doughnut beams (5, 6), and optical tweezers for ultrafine manipulation.

One issue in the creation of a gallium nitride (GaN)-based PC-SEL has been whether a 2D PC structure could be constructed with a sufficient band-edge effect. To do so requires the fabrication of a high-quality 2D GaN/air periodic structure...