

1 Hz and about 100 Hz. In some embodiments, the high-pressure, high-temperature MAS rotors provide a sample spinning rate between about 100 Hz and about 1 kHz. In some embodiments, the 9.5 mm high-pressure, high-temperature MAS rotor provides a sample spinning rate between about 1 kHz and about 3.0 kHz. In some embodiments, the 7.5 mm high-pressure, high-temperature MAS rotor provides a sample spinning rate up to about 5 kHz. In some embodiments, high-pressure MAS rotors with O.D.s less than about 7.5 mm allow sample spinning rates greater than about 5 kHz. In principle, the smaller the rotor O.D., the faster a sample spinning rate that can be achieved. Spinning rates described here are exemplary only.

#### Sample Loading of High Temperature, High Pressure MAS Rotors

A loading chamber detailed, e.g., by Hoyt et al. in US Patent Publication No.: 2012-0146636 may be used to load and seal fluids, gases, and other samples inside MAS rotors of the present invention at a high pressure at room temperature. The loaded rotor may then be transferred to a MAS NMR probe where temperature of the MAS rotors may be increased while positioned within the NMR magnet for in-situ MAS NMR studies.

#### Applications

High temperature, high pressure MAS rotors of the present invention find application in, e.g., catalyst studies, and other applications where high temperatures greater than 100° C. at significantly elevated pressures above about 1.0 atm are employed, e.g., as detailed in the following Example.

#### EXAMPLE

##### Alkylation of Cyclohexanol

In an exemplary catalyst reaction study, <sup>13</sup>C MAS NMR studies on the alkylation of cyclohexanol, a key step in the hydroalkylation pathway, were carried out in-situ. Reaction dynamics/kinetics and role of water were explored using a heterogeneous mixture containing varied amounts of cyclohexanol-1-<sup>13</sup>C and H-Beta zeolite (HBEA) as a function of reaction temperature (up to 163° C.) and reaction time (up to 48 hours). Such analyses can provide such parameters as kinetics and Keq values, provide insights into mechanisms for dehydration including differentiating species adsorbed on the catalyst surface, and species present in the aqueous phase.

FIG. 8 is a plot showing a series of 80 individual <sup>13</sup>C MAS (2.4 kHz) NMR spectra (11.7 T) collected in-situ on a mixture of HBEA (22 mg) and cyclohexanol-1-<sup>13</sup>C (120 μL of 0.33 M) at a high reaction temperature of 163° C. and a high reaction pressure of ~7 atm as a function of time. Spectra were acquired using a recycle delay time of 5 seconds, an accumulation number of 256 scans, and at a sample spinning rate of 2.4 kHz. Acquisition time was approximately 0.29 hours for each spectrum. Quantitative analysis of the spectra in the figure as a function of reaction time yields reaction dynamics/kinetics. For example, relative fractions of both reactants and reaction products as a function of reaction time may be obtained, from which equilibrium constants ( $K_{eq}$ ) and fraction constants ( $K_f$ ) may be calculated. For the analysis, spectral de-convolution was performed first. Then, the integrated peak intensities for either the reactants or the products (e.g., both the species inside the aqueous phase and those in the surface phases) where obtained as a function of reaction time.

Results yielded a ( $K_{eq}$ ) value of 0.43 and a ( $K_f$ ) value of  $3.6 \times 10^{-5} \text{ S}^{-1}$ . FIG. 9a shows a first spectrum taken at time zero from the collection in FIG. 8. A narrow peak at 70 ppm corresponds to cyclohexanol-1-<sup>13</sup>C in the aqueous phase, and a broad peak centered at 70.8 ppm corresponds to the interaction of cyclohexanol-1-<sup>13</sup>C with the H-Beta zeolite surface. Both peaks correspond to the <sup>13</sup>C isotope of the oxygen-bonded carbon of cyclohexanol-1-<sup>13</sup>C. FIG. 9b shows an 80<sup>th</sup> spectrum taken at a time of 22.4 hours into the reaction. A narrow peak at about 125 ppm corresponds to a reaction product in the aqueous phase identified as cyclohexene based on characteristic double bond carbon peaks. A second broad peak located at 126.6 ppm corresponds to the interaction of cyclohexene with the catalyst surface. FIG. 9c shows a migration of the <sup>13</sup>C-labeled carbon isotope in the labeled cyclohexanol molecule during reaction. FIG. 9d shows appearance of new reaction products after a reaction time of 48 hours in the MAS NMR rotor at the same high-temperature (163° C.), high-pressure conditions (~7 atm). In the figure, a benzene dimer and a benzyl ether appear in the spectrum. These in-situ <sup>13</sup>C MAS NMR data show that detailed reaction mechanisms including reaction pathways and reaction kinetics can be obtained for study of catalytic reactions as a function of time.

While a number of embodiments of the present invention have been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the scope of the present invention.

The invention claimed is:

1. A magic angle sample spinning (MAS) nuclear magnetic resonance (NMR) rotor, comprising:

a rotor cylinder composed of a high mechanical strength ceramic with a first inner bore that defines an integrated sample compartment that spans the inner diameter of the rotor cylinder with threads disposed along the inner wall at the upper end of the sample compartment, and a second inner bore that defines an integrated compartment for mounting a spin tip disposed at an end of the rotor cylinder opposite the sample compartment; and a threaded sealing cap with threads that match the threads of the rotor cylinder, the threaded sealing cap is comprised of a high mechanical strength ceramic and configured to secure and compress at least two high temperature gaskets that seal the sample compartment; whereby the integrated sample compartment, gaskets and sealing cap when combined and secured maintain a pressure within the sample compartment of the rotor cylinder of at least up to about 200 atm and a temperature of at least up to about 300° C. without the use of a sealing adhesive.

2. The rotor of claim 1, wherein the rotor cylinder includes a gasket support disposed at an end of the rotor cylinder with a beveled well that supports one of the at least two sealing gaskets and surrounds the opening into the sample compartment of the rotor cylinder.

3. The rotor of claim 1, wherein the gaskets are O-rings and wherein the ceramic sealing cap includes a groove disposed at an end thereof that seats one of the dual O-rings in the rotor cylinder that prevents samples from entering into air gaps disposed between threads of the rotor cylinder and threads of the ceramic sealing cap.

4. The rotor of claim 1, wherein the ceramic sealing cap includes an exposed head or an embedded socket head of a selected shape that enables securing and opening of the sealing cap into or out of the rotor cylinder.