HIGH-PRESSURE, HIGH-TEMPERATURE MAGIC ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE DEVICES AND PROCESSES FOR MAKING AND USING SAME

CROSS REFERENCE TO RELATED APPLICATION

This application is a non-provisional application that claims priority from U.S. Provisional Application No. 61/680,958 entitled "Devices for Combined High Temperature and High Pressure Magic Angle Spinning Nuclear Magnetic Resonance", filed 8 Aug. 2012, which reference is incorporated herein in its entirety.

STATEMENT REGARDING RIGHTS TO INVENTION MADE UNDER FEDERALLY-SPONSORED RESEARCH AND DEVELOPMENT

This invention was made with Government support under contract DE-AC05-76RLO1830 awarded by the U.S. Department of Energy, and the National Institute of Environmental Health Sciences under contract R01ES022176 awarded by the National Institutes of Health. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates generally to magic angle spinning (MAS) nuclear magnetic resonance (NMR) devices for spectroscopy. More particularly, the present invention relates to combined high-pressure, high temperature magic angle spinning rotors and processes for machining ceramic components of rotors for high-pressure, high temperature magic angle spinning nuclear magnetic resonance spectroscopy.

BACKGROUND OF THE INVENTION

High resolution magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy is a powerful and versatile technique for studying molecular structure and dynamics in solid systems, semi-solid systems, or heterogeneous systems containing mixtures of e.g., solid, semi-solid, liquid, and gaseous phases. Thus MAS NMR is an attractive tool for in-situ investigations of reaction dynamics and intermediates, investigations of properties of active sites in catalysts during catalytic conversion of biogenic molecules in aqueous phase water, and physical/chemical properties and/or phase transitions in materials and material syntheses. However, reusable sample cells that perform well at temperatures greater than about 100° C. and pressures greater than the vapor pressure of aqueous water have not been realized in MAS NMR to date due primarily to technical difficulties associated with sealing heterogeneous fluid samples at high temperature and high pressure conditions that would prevent leakage of fluids while spinning samples at a spinning rate of several kHz or more inside a strong magnetic field. To date, MAS NMR experiments have been performed at pressures of about 150 bar and temperatures up to 80° C. using a zirconia rotor sleeve and plastic components including bushings, O-rings, valves, and valve adaptors detailed, e.g., by Hu et al. in "High-Pressure Magic Angle Spinning Nuclear Magnetic Resonance", *J. Magn. Reson.,* 212, 378-385 (2011); Hu et al. in "Rotor Design for High Pressure Magic Angle Spinning Nuclear Magnetic Resonance", *J. Magn. Reson.,* 226, 64-69 (2012); and US Patent Publication No.: 2012/0146636. However, plastic components soften at higher temperatures, rendering previous designs unsuitable at temperatures above 100° C. Accordingly, new rotor designs are needed that provide sealing of heterogeneous fluid samples at high temperature and high pressure conditions and prevent leakage of fluids while spinning samples at spinning rates of several kHz or more inside strong magnetic fields. The present invention addresses these needs.

SUMMARY OF THE INVENTION

The present invention includes new high temperature and high pressure Magic Angle Spinning (MAS) rotors that generate high-resolution NMR spectra in operation at high pressures and high temperatures. These exemplary new designs make a variety of combined high temperature and high pressure MAS NMR experiments possible that were previously not possible. Exemplary MAS rotors are detailed herein with outside diameters (O.D.) of 9.5 mm, 7.5 mm, and 5 mm, respectively. However, rotor diameters are not limited. For example, rotors with O.D. dimensions greater than 9.5 mm and less than 5 mm may be fabricated as detailed herein including rotors with outside diameters of, e.g., 4 mm, 3.2 mm, or smaller diameters, albeit with increasing fabrication difficulty as dimensions decrease. The MAS rotors are reusable and provide ^{13}C background-free operation at temperatures at least up to 300° C. and pressures at least up to 200 atmospheres or greater. When sealed, the rotor maintains a selected high pressure and high temperature within the sample cell without release of fluids and gases from the materials therein. The new capability makes possible a variety of high temperature and high pressure MAS NMR analyses and experiments that were previously impossible including, e.g., in situ MAS NMR analyses of reactions, materials, fluids, and gases.

Rotor volumes are not limited. Dimensions of the rotor determine the possible volumes that can be used. Thus, no limitations are intended by the description of exemplary embodiments disclosed herein. In some applications, volumes may be at least up to about 75 μL. In some applications, volumes may be up to about 250 μL. In some applications, volumes may be up to about 500 μL. In some applications, volumes may be up to about 750 μL or greater.

In one design, the MAS rotor may include a reusable rotor cylinder composed of a ceramic such as zirconia. In some applications, the rotor cylinder may include a width dimension (O.D.) of 9.5 mm with a smooth inner surface along the length of the inner wall. A rotor sleeve insert, e.g., with a cylindrical shape and a single opening at a top end of the insert may be introduced into the rotor cylinder along the length of the inner wall of the rotor cylinder. The rotor sleeve insert may be made of a machinable glass ceramic such as MACOR® (Corning Glass Inc., Corning, N.Y., USA) composed of fluorphlogopite mica in a borosilicate glass matrix, or other suitable materials. When introduced into the rotor cylinder, the rotor sleeve insert may form a sample compartment into which samples may be introduced and sealed in the MAS rotor. The rotor sleeve insert may be secured inside the rotor cylinder with a thin layer of a high strength, high temperature glue such as Aremco-Bond 631-B-1108 epoxy (Aremco Products, Inc., New York, N.Y., USA) positioned between the outer surface of the rotor sleeve insert and the inner wall of the rotor cylinder that prevents release of the rotor sleeve insert from the rotor cylinder during sample spinning. In the instant design, since the sample compartment is inside the rotor