

17

between two layers of glass wool and ceramic end plugs inside the CF-MAS rotor. Sample temperature was calibrated using ^{207}Pb MAS NMR using a solid powder of $\text{Pb}(\text{NO}_3)_2$ at a sample spinning rate of 3.5 kHz. To ensure temperature accuracy, sample spinning rate, flow rate of the N_2 heating gas, and the driving and bearing nitrogen gas pressures were the same as those employed for the calibration of the ^{207}Pb MAS NMR experiment.

EXAMPLE 3

Theoretical Calculations and Methods

Density function calculations were performed using the Amsterdam Density Functional (ADF®) program for molecules (Scientific Computing & Modelling, Amsterdam, Netherlands). Geometries were optimized and isotropic chemical shielding values of the chemical shielding tensor were calculated at the BLYP/QZ4P level of theory. Under these conditions, the calculated ^{13}C isotropic chemical shielding value for $\text{Si}(\text{CH}_3)_4$ (TMS) was 176.3 ppm. Shielding values were converted to the experimental chemical shift scale relative to TMS (0 ppm) according to δ (ppm) = $176.3 \text{ ppm} - \delta_{\text{calculated}}$ (ppm).

EXAMPLE 4

Sensitivity and Temperature Test

Using adamantane as a test sample, sensitivity of the 9.6 mm (ID of 8 mm) large-sample-CF-MAS probe was found to be approximately 2 times that of a standard commercial 7.5 mm (I.D. of 6 mm) CP/MAS probe using a tightly packed sample cylinder of approximately 10 mm in height for both cases. Sensitivity enhancement is consistent with the expected volume increase, suggesting that the sensitivity of the 9.5 mm CF-MAS probe meets expectations. Using a home-made heating stack, under the conditions of VT N_2 gas flow of 70 L/min, driving N_2 gas pressure of 32.5 psi, bearing N_2 gas pressure of 37.3 psi, a stable sample spinning rate of 3.5 kHz was reached and a temperature up to 230° C. was achieved.

EXAMPLE 5

Validating Flow in the Catalyst

Gases can flow through a tube containing porous catalysts as long as there is a pressure difference at the two ends of catalyst bed. Flow rates and patterns inside the catalyst bed can depend on factors such as the value of the pressure difference at both ends of the catalyst bed, thickness of the catalyst, properties of both the internal (i.e., the intrinsic pore structures of the catalysts) and external structure (i.e., the space distribution between the catalyst particles), properties of the gases and operation temperatures, and etc. Experiments were carried out to validate existence of flow in the catalyst located within the sample chamber of the CF-MAS NMR rotor, those with a vacuum pump (e.g., a Diaphragm Membran-Vakuum Pumpe with a maximum 1.7/2.0 m³/hour capacity from BrandTech Scientific, Inc., Essex, Conn., USA) turned on and those without a vacuum pump turned on. Meso-silicalite-1 is inert to 2-butanol at 73° C. Thus, in situ CF-MAS ^1H NMR experiments with and without the vacuum pump turned on were carried out on the catalyst as a function of time by flowing 2-butanol at a rate of 1.5 mL liquid/hour at this temperature. 2-butanol was injected/mixed into a flow of

18

dry N_2 carrier gas at room temperature using a combination of a syringe pump and a mass flow controller positioned outside the NMR superconducting magnet before flowing into the sample chamber of the CF-MAS NMR probe. Flow rate of the carrier gas was set at 100 sccm. Results are shown in FIG. 5a. Data show that the integrated peak intensity at equilibrium when the vacuum pump is on is lower than when the vacuum is off. This can only be possible if a flow is formed inside the catalyst bed. For an idea gas, it is well known that $P=(n/V)\times R\times T$, where P is the pressure, R is the universal gas constant, T is the temperature in K, and (n/V) is the number of mole of gas molecules per unit volume. When the vacuum pump is off, P is about 1 atm everywhere inside the catalyst bed. When the vacuum pump is on, P decreases linearly from 1 atm at the injection end of the catalyst to nearly zero at the exit end of the catalyst, where the vacuum pump is attached, which causes a linear drop in pressure drop inside the catalyst. T is almost constant across the catalyst, which gives a linear decrease in the value of (n/V) across the catalyst. Total quantity of 2-butanol decreases, resulting in a decrease in the integrated peak area at equilibrium when the vacuum pump is on. Integrated peak intensity only decreases by about 15%, indicating that a major portion of 2-butanol remains inside internal pores of the catalyst, which is affected less by flow due to the confined pore structures. 2-butanol molecules located in inter spaces between catalyst particles is most affected by flow. Diffusion allows for exchange of molecules inside the inner pores of the catalysts with molecules located in the spaces between the catalyst particles.

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 invention.

What is claimed is:

1. A nuclear magnetic resonance (NMR) probe for high resolution in situ NMR investigations, the probe comprising:
 - a magic angle spinning (MAS) rotor that defines a sample chamber with an internal volume greater than or equal to about 0.01 cm³ configured to contain and rotate a catalyst or a solid therein;
 - a first (top) end plug disposed above the sample chamber comprising an introduction tube that couples to at least three inlets, the inlets are configured to introduce a carrier gas containing one or more reactants or a mixture thereof to a catalyst or a solid within the sample chamber at a pressure at or above atmospheric pressure;
 - a second (bottom) end plug disposed below the sample chamber comprising an exit tube that couples to at least three outlets, the outlets are configured to collect one or more reaction products when released from the catalyst or solid within the sample chamber at a pressure below atmospheric pressure; and
 - a spin (drive) tip disposed below the second end plug through which the exit tube from the second end plug extends, the exit tube delivers the one or more reaction products collected from the sample chamber in the at least three outlets as the rotor rotates, the exit tube couples operatively to a vacuum pump or device disposed external to the rotor that maintains the pressure difference between the inlets and outlets within the rotor.
2. The probe of claim 1, wherein one of the at least three inlets is centrally disposed.
3. The probe of claim 1, wherein the at least three inlets are configured to deliver the carrier gas containing the one or