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**MAGIC ANGLE SPINNING NUCLEAR
MAGNETIC RESONANCE APPARATUS AND
PROCESS FOR HIGH-RESOLUTION IN SITU
INVESTIGATIONS**

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. 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) spectroscopy. More particularly, the present invention relates to a new large volume, continuous-flow MAS rotor, probe, and process that permit magic angle spinning nuclear magnetic resonance spectroscopic investigations in situ.

BACKGROUND OF THE INVENTION

Understanding mechanisms of reactions on catalysts requires the nature of active sites of the catalyst and the dynamic processes of the reactions to be understood starting when reactants enter the reaction zone, reaction intermediates begin to form, until final eluted reaction products exit the catalyst reaction system. For reactions involving simple species, in-situ techniques such as UV-visible and IR spectroscopies are typically used to probe the intermediates adsorbed on the catalyst. However, for reactions such as selective oxidations of organics, where reaction products and intermediates are complex, a single spectroscopic tool is insufficient. High resolution magic angle spinning (MAS) nuclear magnetic resonance (NMR) is a powerful and versatile technique for studying molecular structures and reaction dynamics regardless of whether the system under investigation is a solid, semi-solid, or a heterogeneous system containing mixtures of e.g., solid, semi-solid, liquid, and gaseous phases. While a number of in situ MAS NMR techniques have been developed to study heterogeneous catalysts, MAS investigations of catalyst reactions in situ have not yet been reported for MAS rotors with diameters larger than 7.5 mm due to technical challenges associated with sensitive detection of reactions occurring in shallow layers of catalyst beds placed in large bed volumes. The present invention addresses these needs. Additional advantages and novel features of the present invention will be set forth as follows and will be readily apparent from the descriptions and demonstrations set forth herein. Accordingly, the following descriptions of the present invention should be seen as illustrative of the invention and not as limiting in any way.

SUMMARY OF THE INVENTION

A Continuous-Flow (CF) Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) rotor, probe, and process are detailed that provide for high-resolution NMR investigations of reaction dynamics, stable intermediates/transition states, and mechanisms of catalytic reactions in situ. The term "rotor" as used herein means a catalyst or solid holding device that inserts into a MAS NMR probe allowing in situ investigations or analyses involving the catalyst or solid. The

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term "probe" refers to the analysis instrument for conducting CF-MAS NMR investigations. The term "continuous flow" (CF) means that the introduction of carrier gas and/or reactants in a carrier gas is performed at a constant flow rate, but the rotor and probe are not limited to CF applications. For example, in some applications, stop-flow investigations can be conducted. Thus, no limitations are intended.

The magic angle spinning (MAS) nuclear magnetic resonance (NMR) rotor for high resolution in situ NMR investigations described herein includes a sample chamber with an internal volume greater than or equal to about 0.01 cm³ that is configured to contain and rotate a catalyst or solid. Rotation of the catalyst or solid within the sample chamber may be synchronized with the rotation of the MAS rotor.

Rotor sizes are not limited. Rotor diameters may vary from about 3 mm to about 14 mm. In some applications, rotor diameters may be below 5 mm. In some applications, rotor diameters may be about 3.2 mm. In some applications, rotor diameters may be above 5 mm, e.g., 9.5 mm. No limitations are intended.

The MAS rotor may also include an introduction member that is operatively coupled to the sample chamber and configured to actively deliver zero reactants, one or more reactants, or mixtures of reactants into the catalyst at a pressure preferably about atmospheric pressure. However, pressures are not limited. For example, pressures through the introduction tube member may be from about 670 mm Hg to about 870 mm Hg. The term "actively delivered" as used herein means flow of reactants into or through the catalyst occurs under a driving force arising from a pressure difference at respective ends of the catalyst inside the sample chamber. The introduction member when assembled inside the MAS rotor may be enclosed within an end plug member that couples operatively to the sample chamber via one or more through-holes positioned above and that circumscribe the sample chamber and configured to deliver the one or more reactants introduced through the introduction member into the sample chamber at the top along the periphery of the catalyst therein. The introduction tube member may also couple to at least one through-hole positioned centrally above the sample chamber to deliver reactants into the catalyst at the top of the sample chamber. The end plug may comprise a ceramic or a plastic and be positioned at an end inside the MAS rotor above the catalyst and configured to rotate along with the catalyst located within the sample chamber as the MAS rotor rotates while the introduction member remains stationary.

The opening of the introduction tube at the end toward the catalyst may include a spread design in which the tube narrows in internal diameter and then expands to deliver a spray of reactants into the catalyst. The opening may couple to a single through-hole in the end plug. The end plug member may comprise a ceramic or a plastic that is positioned at an end inside the MAS rotor above the catalyst and configured to rotate along with the catalyst located within the sample chamber as the MAS rotor rotates while the introduction member remains stationary. The term "stationary" used herein with reference to the introduction tube member and the exit tube member means these components do not rotate inside the MAS NMR probe and are fixed in space.

The MAS rotor may also include an exit member that couples operatively to the sample chamber that is located at an end opposite the introduction tube member and configured to actively remove one or more products from the catalyst at a pressure below atmospheric pressure. For example, pressures through the exit tube member may be from about 0.1 mm Hg to about 760 mm Hg. No limitations are intended. The exit member when inside the MAS rotor may be enclosed