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A Nuclear Magnetic Resonance Probe for *in Situ* Studies of Adsorbed Species on Catalysts

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INTRODUCTION

The use of nuclear magnetic resonance (NMR) spectroscopy to study adsorbed species on catalyst surfaces has grown rapidly in the last 10 years (*1*). The motion and structure of adsorbates can now be studied in detail by applying sophisticated time and excitation phase dependent techniques. To date, most investigators have prepared their samples *ex situ* in a sealed tube that can be placed in the coil of the NMR probe (*2*). While simple, this technique is inconvenient for studying the effects of adsorbate pressure and adsorption temperature. A more flexible arrangement involves sample cells that can be attached to a volumetric adsorption apparatus (*4, 5*), or gas feed system (*3*). Using this approach, it is possible to alternate static adsorption and NMR measurements, or to do batch reactions. In the present paper we describe a double resonance NMR probe with a built-in microreactor that can be heated or cooled. This design permits investigations of steady-state catalytic reactions, as well as static adsorption experiments.

DESCRIPTION OF THE NMR PROBE

An illustration of the probe and its component parts is shown in Fig. 1. The probe body is a 4-in.-outer-diameter aluminum tube, chosen to fit into the 4-in. bore of a 4.2-T (180-MHz proton resonance) superconducting magnet. The large diameter of the probe allows for enclosure of the resonant circuit and the sample cell.

The circuit used to apply rf power and to detect the NMR signal is a single coil arrangement commonly used for double resonance experiments with solids and is shown in Fig. 2. Similar circuits are presented in Refs. (*6*) and (*7*). Approximate resonance conditions for this circuit can be arrived at using a simple node analysis and are as follows:

$$\omega_{\text{high}}^2 \cong \frac{1}{C_1}\left(\frac{1}{L_1}+\frac{1}{L_2}\right) \tag{1}$$

$$\omega_{\text{low}}^2 \cong \frac{1}{C_2 L_1}, \tag{2}$$

where C_1 and C_2 are the respective low-frequency (18 MHz) and high-frequency (180 MHz) tuning capacitors (obtained from Polyflon, see Ref. (*8*)), and are externally tunable (see Fig. 1a). L_1 is the free standing sample coil. The large diameter of L_1 is necessary to achieve a sampling volume which can contain greater than 10^{19} NMR active nuclei. Large samples are necessary in studies of adsorbates since the NMR active nuclei are confined to the surface of the material. To eliminate background ^{1}H signal due to traces of solder flux, L_1 is connected mechanically to the rest of the resonant circuit. Heating and cooling considerations result in a probe geometry that requires L_1 have rather long leads. This creates high-frequency tuning problems, because of the extra inductance (*9*). L_2 alleviates this tuning problem, but at the expense of power dissipation in L_1. Rough tuning of the high-frequency part of the circuit can be accom-

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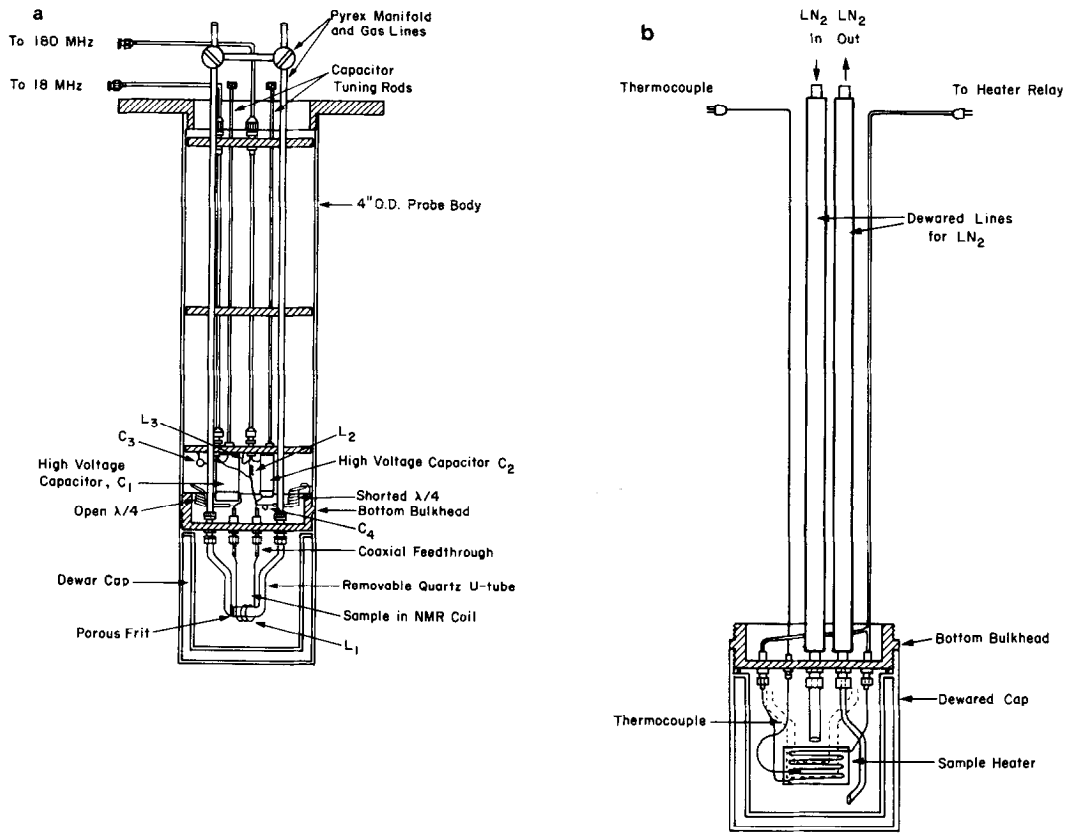
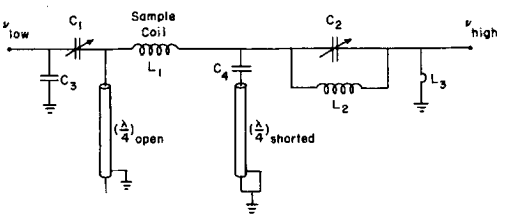


FIG. 1. *In situ* NMR probe. (a) Showing the gas flow system and the resonant circuit. (b) Showing heating and cooling system components.

plished by changing the length of L_2. Nichrome wire was used to supply the necessary real part of the impedance for the high-frequency circuit to give a low Q (~70) and thus shorten the ringdown time. (For the ^1H circuit, ringdown is typically equal to the 90° pulse length, 4 μs.) Fifty-ohm impedance matching is performed at high and low frequencies by L_3 and C_3, respectively. The quarter-wave traps are constructed of 50 Ω solid copper coaxial cable with Teflon dielectric. The cables are cut to length by maximizing the attenuation of a 180-MHz signal. The open quarter-wave cable displays low impedance at 180 MHz but very high impedance at 18 MHz, effectively isolating the high-frequency circuit from the low-frequency input. The combination of C_4 and the closed quarter-wave shows high impedance at 180 MHz but low impedance at 18 MHz, isolating the low-frequency circuit from the high-frequency input. (C_4 and the shorted quarter-wave cable comprise a high Q series resonant trap circuit at 18



C_1 - 5 to 25 pf Polyflon in parallel with 450 pf ceramic
C_2 - 0.8 to 10 pf Polyflon
C_3 - 800 pf ceramic
C_4 - 815 pf ceramic
L_1 - 5 turns, 10 mm I.D., 15 mm long, flattened No. 18 copper wire, 0.25 μH at 18 MHz
L_2 - 7 turns, 5 mm I.D., 20 mm long, nichrome wire
L_3 - "Omega" shaped, No. 16 flattened copper wire

FIG. 2. Double resonance circuit.

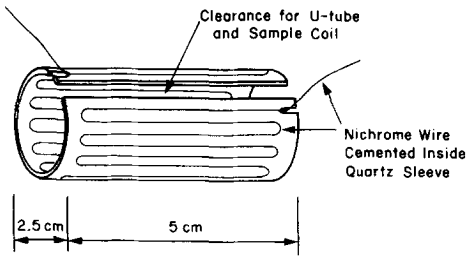


FIG. 3. Heater element.

MHz.) Isolation is greater than 30 dB in both directions. Further isolation is provided by 18- and 180-MHz bandpass filters on the rf inputs.

The reactor is a quartz U-tube with a porous frit in the 10-mm-o.d. horizontal section to hold the catalyst in place. Quartz wool is packed in the other end of the catalyst bed after the catalyst is loaded. The reactor is connected to quartz inlet and outlet tubes via Cajon Ultra-Torr unions welded into the bottom bulkhead of the probe. The gas handling lines are then connected to a Pyrex manifold outside the probe body. The manifold permits flushing the gas flow system up to the sample, bypassing the catalyst, or closing off the sample in a vacuum or gaseous atmosphere. The manifold inlet can be attached to either a gas feed apparatus or static adsorption apparatus, while the outlet can be routed to a gas chromatograph to measure reaction product concentrations.

The furnace used for heating consists of nichrome wire cemented inside a quartz sleeve which surrounds the sample and NMR coil. The heater element is shown in Fig. 3. This configuration was chosen to minimize inductive coupling between the NMR circuit and the heater. The heater leads feed through the bottom bulkhead and exit at the top of the probe, where they connect to a relay that is driven by a port on the spectrometer pulse programmer. The heater control is provided by a proportional band temperature controller in line with a Variac which is connected to the other side of the relay driven by the pulse programmer (see Fig. 4). Thermocouples for temperature control and measurement also feed through the bottom bulkhead. Both thermocouple junctions are located inside the heater and approximately 2 mm from the outside of the sample coil.

A signal from the NMR pulse programmer to the relay holds the relay open (no power to heater) during the application of radio frequency power to the sample coil and signal acquisition. The heater is turned off 50 ms prior to pulsing to prevent heater transients from affecting the FID. This de-

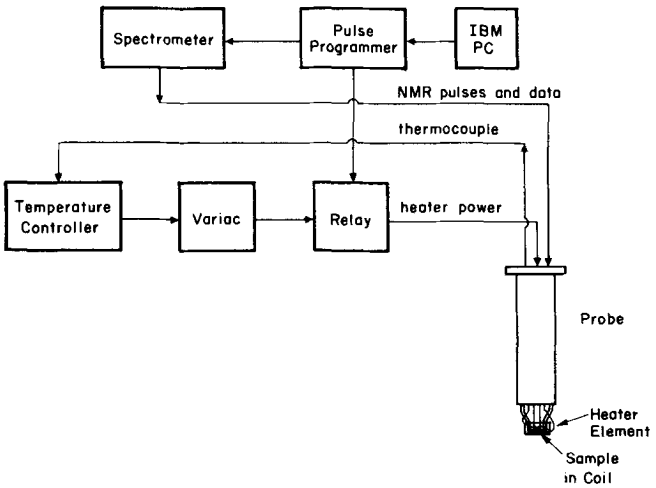


FIG. 4. Heater control system.

lay could be shortened, since the heater is a purely resistive circuit and has a short ringdown time (~10 ms). The field produced by the heater solenoid (<0.01 T) is negligible compared to H_0 (4.2 T). As long as the pulsing and acquisition time is short compared to the time between NMR experiments, this heating scheme will work well. For example, the observation of surface ^1H on catalysts with a 90° pulse–observe sequence typically involves a total pulse and acquisition time of less than 10 ms. T_1 is typically 1 to 2 s, and to allow complete spin–lattice relaxation it is necessary to wait 5 to 10 s between 90° pulse–observe experiments. Since the heater only needs to be off during the less than 10-ms pulse and acquisition time, the sample can easily be maintained at constant temperature.

For *in situ* operation, the upper temperature limit is governed by the melting point of the sample coil material (for Cu, T_m = 1082°C), since the sample coil is connected to the rest of the circuit without solder. It is unlikely, though, that measurements could be made at temperatures this high due to low signal-to-noise and possible heating of the magnet bore.

Cooling of the sample is achieved by passing liquid nitrogen or cooled dry nitrogen gas through dewared ¼-in. lines (see Fig. 1) to a dewared cap surrounding the reactor and sample coil. When using liquid nitrogen, the outside of the probe near the bottom bulkhead reaches ~0°C because of the conduction path from the inner dewar wall to the outside of the probe. Excessive cooling of the magnet bore can be reduced by blowing dry nitrogen gas at room temperature through the electronics section of the probe. Since the electronics for the probe circuit are isolated from the sample chamber, there is no temperature-induced detuning of the circuit over a wide temperature range at the sample.

The probe design described here has been used in our laboratory to obtain relaxation time measurements and spectra for ^1H in H_2 and NH_3 chemisorbed on high surface

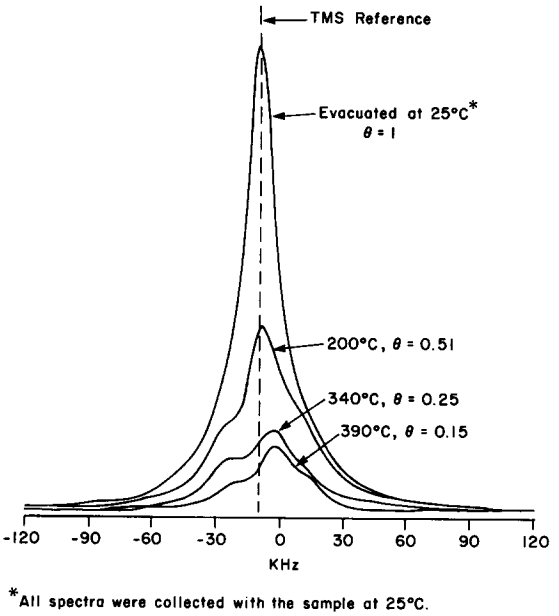


FIG. 5. Time-interupted TPD–NMR spectra of NH_3 on γ-Mo_2N.

area (120 m^2/g)γ-Mo_2N (*10*). NMR measurements at 77 K have been made, and catalyst treatments up to 700°C (outside magnet) have been performed in the probe. Figure 5 shows a series of ^1H spectra taken following room-temperature adsorption of NH_3 on γ-Mo_2N and heating to progressively higher temperatures under vacuum. The interpretation of these spectra is discussed in Ref. (*10*).

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