Nuclear Magnetic Resonance (NMR) Relaxometry Investigations of Cu-ZnO/Al_2O_3 Catalysts used in syngas-to-methanol conversion

Allison Hermelink

Dr. Klaus Woelk

Department of Chemistry

4/4/2022

Abstract

Methanol is an important raw material for many industrial and laboratory processes. It is synthesized by converting natural gas to a mixture of carbon monoxide and hydrogen gas. This mixture, called syngas, is then converted with help of a Cu-ZnO/Al_2O_3 catalyst to produce methanol. Only about 7% of methanol is yielded in a one-turn conversion. NMR relaxometry will be conducted in a specialized toroid-cavity probe to better understand the reactivity of the active sites of the catalyst. The toroid-cavity probe can record NMR relaxation times under industrial reaction conditions. A computational algorithm will be used to analyze multiexponential decay data and extract their correlated relaxation times. The relaxation times are associated with chemical environments for different reactive components of the methanol synthesis, such as freely moving molecules versus locally fixed molecules. The relaxometry results are used to identify yield-inhibiting processes such as water deposition on the catalytically active sites.

Introduction

Methanol (CH_3OH) is an important bulk material used in many industrial and laboratory processes. Acetic acids, formaldehyde, gasoline and its common additive MTBE (methyl tert-butyl ether), as well as many other chemicals are made from methanol [1]. Natural gas (CH_4) is typically the starting material for the methanol synthesis for it produces less greenhouse gases than similar syntheses from coal or petroleum. In the natural gas to methanol conversion, natural gas is first reacted by steam reforming to yield syngas ($CO + H_2$), which is then converted to methanol using a catalyst made from copper, zinc, and aluminum oxide ($Cu\text{-}ZnO/Al_2O_3$). On the industrial scale, the maximum theoretical once-through conversion rate is about 55%-75% when using temperatures of 200-300 °C and syngas pressures of 35-100 atm. Heat management can improve the once-through conversion by about 10%, and water-cooled reactor designs can achieve even higher conversion rates. However, a minimum of three to four recycle reactions are still needed even with the water-cooled reactor design [2]. Overall, the syngas to methanol per-pass conversion is only about 25% efficient. Other reactions pathways known for the methanol synthesis may have higher conversion efficiencies, but they are currently too expensive to be economically attractive [3]. In this research project, Nuclear Magnetic Resonance (NMR) relaxometry in a toroid-cavity pressure probe is used for the first time to study interactions of CH_4 with the $Cu\text{-}ZnO/Al_2O_3$ catalyst under industrial reaction conditions. This pioneering NMR work is expected to lead to future research that may be able to identify interfering factors that cause the low conversion rates for the natural gas to methanol conversion.

Toroid-Cavity NMR Probe

A toroid-cavity NMR probe contains a non-magnetic, cylindrical pressure vessel as the sample container. It is a specialized NMR device that combines a pressure vessel with the NMR resonator in one structural element (Fig. 1). Constructed in this unique way, it can be used for in situ NMR spectroscopy at temperatures up to 250 °C and pressures up to 200 atm [4]. The toroid-cavity pressure vessel used in this study is similar to the one shown in Fig. 1. and is made from diamagnetic phosphor bronze with an inner hollow central conductor of copper-beryllium alloy. The hollow central conductor is not only used to apply radiofrequency pulses to the sample and record NMR resonances, but also to introduce gaseous components into the vessel and monitor their pressure. A heating jacket around the pressure vessel and a thermocouple wire inserted from the bottom are additional components that provide for accurate temperature control and monitoring.

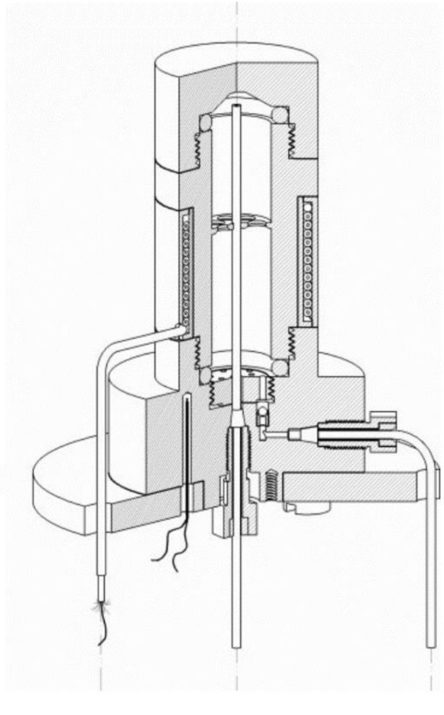

Figure 1: Toroid Cavity NMR Probe for high-pressure and high-temperature NMR investigations. Image taken from ref. [4].

NMR Relaxometry Pulse Sequences

At thermodynamic equilibrium, the net magnetization of NMR-active nuclear spins is aligned with the main magnetic field of the NMR spectrometer. When a radiofrequency pulse is applied, it turns the net magnetization away from the direction of the main magnetic field. After the completion of the radiofrequency pulse, the net magnetization will relax back to thermodynamic equilibrium by two independent processes termed spin-spin and spin-lattice relaxation. Spin-spin relaxation refers to interactions between individual nuclear spins, which result in a loss in phase coherence, while spin-lattice relaxation is caused by an energy exchange of nuclear spins with its surroundings (i.e., the lattice). Both spin-spin and spin-lattice relaxation depend strongly on the local chemical environment around the NMR-active nuclei, which makes NMR relaxometry an important technique to investigate such environments. A nuclear spin will relax at a faster rate if the mobility within the molecule is restricted, if the mobility of the entire molecule is restricted, such as by adsorption on solid surfaces, and if paramagnetic impurities are present.

The typical NMR experiment to observe spin-lattice relaxation is called inversion-recovery experiment. In this experiment, a 180° radiofrequency pulse turns the net magnetization of the sample upside-down, such that it is aligned 180° against the magnetic field of the NMR spectrometer (i.e., it is inverted). The inverted magnetization then recovers toward its thermodynamic equilibrium where it is again aligned with the direction of the spectrometer's main magnetic field. In the inversion-recovery experiment, the radiofrequency inversion pulse is followed by a variable recovery time before the magnetization is recorded by an observe pulse and a signal acquisition time. By varying the recovery time, a series of NMR spectra is recorded in which the signal intensities are functions of the recovery time. The recovery-time dependent signal intensities are evaluated by a computational algorithm which is an Inverse Discrete Laplace Transform, that reveal relaxation rates (R_1) or relaxation time constants ($T_1 = 1/R_1$).

NMR relaxometry is of particular interest in investigations where chemical shift, the parameter typically used for analyzing molecular structures, doesn't reveal the desired information. For example, when chemical-shift information is obstructed by very broad spectral lines, NMR relaxometry can still distinguish between different species based on their different relaxation rates or relaxation time constants.

Experiments

To perform the desired methane gas relaxometry experiments in the toroid-cavity NMR probe, a pressure station was set up and a pressure manifold implemented. The methane pressure tank was equipped with a special high-pressure regulator (0-200 atm) to control the pressure in the toroid-cavity probe up to 100 atm. Standard regulators only allow gases to be retrieved up to 40 atm, which was not sufficient for this study. Stainless-steel tubing with an outer diameter of 1/16" was used to connect the regulator to a pressure manifold and the manifold to the toroid-cavity probe. The manifold consists of a pressure transducer for monitoring the pressure and two valves, where one is to fill gas into the probe and the other one to purge gas from the probe. The toroid-cavity pressure probe was initially tested with 45.5 µL of water. The water sample was inserted into the sample area of the toroid-cavity probe to calibrate the NMR resonance frequency, homogenize (i.e., shim) the magnetic field, and optimize the transfer of radiofrequency pulses to the sample. The probe was then cleaned and re-charged with methane gas up to 50 atm. A leak test was conducted with a mixture of soap and water to make sure the manifold and the probe were completely gas tight. Finally, the electrical heating jacket that surrounds the toroid-cavity pressure vessel was tested by applying temperatures up to 60 °C to the sample container while the sample was under 40 atm of pressure.

As the next step, a series of experiments was conducted to test the toroid-cavity probe performance with respect to relaxation-time measurements. It is long known from the literature [4, 5] that spin-lattice relaxation times of gases depend strongly on the pressure. For example, Fig. 2 shows the pressure dependence of the spin-lattice relaxation time (longitudinal relaxation time) for methane gas. In our own investigations a modified inversion-recovery NMR pulse sequence was applied to methane gas inside the toroid-cavity probe at pressures of 1 atm, 5 atm, 10 atm, 15 atm, 30 atm, and 45 atm. The relaxation times calculated from ^{1}H-NMR methane signal intensities as a function of recovery times confirmed that the toroid-cavity probe can reproduce the relaxation-time data from the literature to within ± 2%.

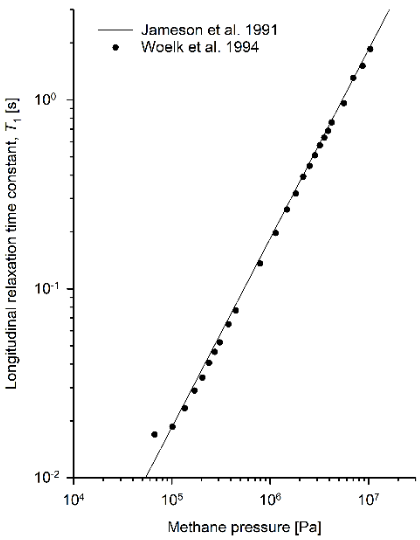

Figure 2: Pressure dependence of the spin-lattice relaxation times of methane gas at a temperature of 300 K. Modified version of a plot obtained from ref. [4].

A sample of Cu-ZnO/Al_2O_3 catalyst obtained from BASF (Ludwigshafen, Germany) was ground into a powder by a mortar and pestle. Grinding the pelleted solid BASF catalyst into a fine powder makes it possible to add more material into the toroid-cavity sample container and distribute it homogeneously across the sample area. A sample of 4.106 g of the ground catalyst was compacted into the toroid-cavity sample container, and the pressure probe closed and sealed. A pressure of 23.8 atm of methane was applied through the stainless-steel tubing and continuously monitored by the manifold's pressure transducer. A series of 128 inversion-recovery experiments were conducted with varying recovery delays between $t_{\min} = 5\times10^{-5}$ (50 µs) and $t_{\max} = 5$ s. The recovery times were equally spaced between $t_{\min}$ and $t_{\max}$ on a logarithmic recovery-time scale according to the following equation:

$$t_i = t_{\min}{}^{\left(\frac{128-i}{127}\right)} \times t_{\max}{}^{\left(\frac{i-1}{127}\right)} \qquad i = \{1, 2, 3, \ldots, 128\}$$

Consecutive experiments were carried out with the same parameter set except with the methane pressure set at 18.3 atm, 12.5 atm, 6.7 atm, 0.96 atm. Removing methane gas from the toroid-cavity sample container in order to reduce the gas pressure was done very slowly, so that the catalyst powder did not get disturbed inside the probe or flushed back into the stainless-steel tubing.

A typical NMR spectrum, recorded from the methane gas added to the catalyst inside the toroid-cavity probe is shown in Fig. 3. The ^{1}H-NMR signal of methane is broadened substantially by the paramagnetic compounds contained in the catalyst. Particularly, the paramagnetic Cu^{2+} ions in the catalyst concentrate the magnetic field in their immediate vicinity and, thus, modify the resonance frequency of the hydrogen atoms in methane. The methane signal linewidth is broadened to 35 ppm, while it is observed at 0.085 ppm without the presence of the catalyst. In Fig. 3, the wide-line NMR spectrum of methane in the presence of the catalyst is compared with the signal without the catalyst. The vertical gray bar in Fig. 3 indicates the spectral range (i.e., the chemical-shift range) that is typically used for ^{1}H-NMR spectroscopy of organic molecules. To capture the entire methane signal in the presence of the catalyst, a 75-fold expansion of the chemical-shift range was needed.

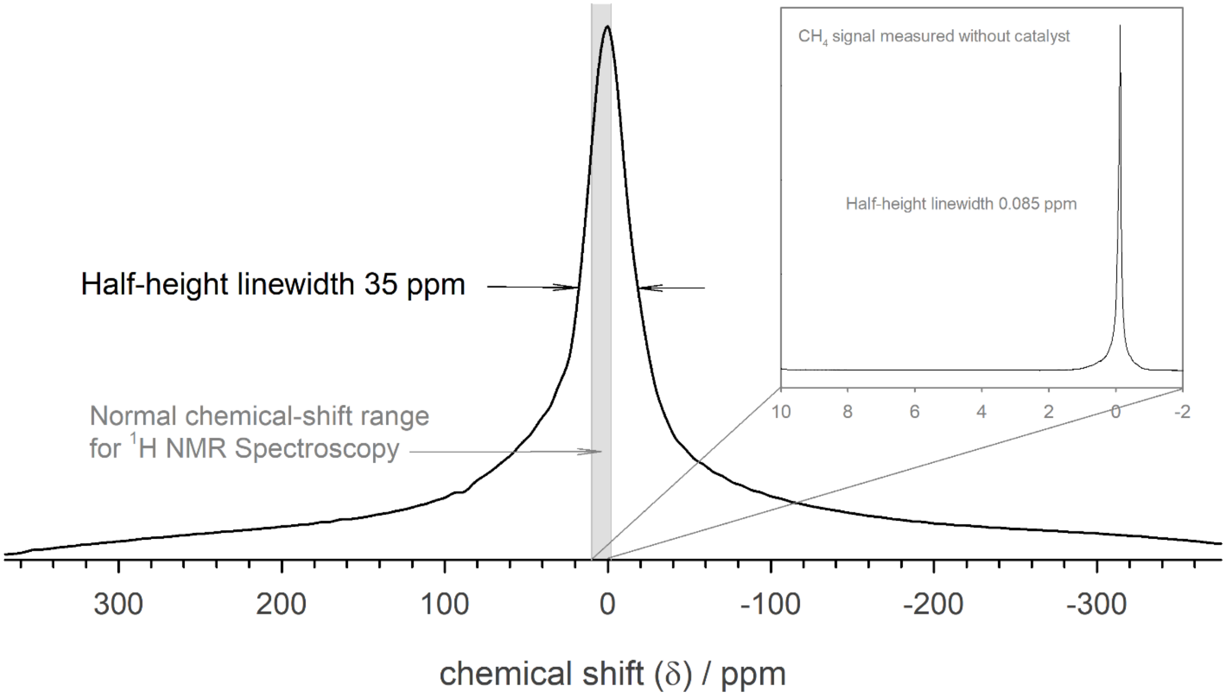

Figure 3: ^{1}H-NMR wide-line spectrum of CH_4 and Cu-ZnO/Al_2O_3 catalyst at 23.8 atm in a toroid-cavity NMR probe. The vertical gray bar indicates the chemical-shift range that is typically used in ^{1}H-NMR spectroscopy. The inset shows the narrow linewidth obtained from methane gas at 23.8 atm without the presence of the Cu-ZnO/Al_2O_3 catalyst.

After the five series of 128 inversion-recovery experiments (23.8 atm, 18.3 atm, 12.5 atm, 6.7 atm, and 0.96 atm) were completed, the results of the numerical algorithm mentioned above indicated relaxation time constants between T_1 = 2 µs and T_1 = 2 s. In a refined series of inversion-recovery experiment, 256 different recovery times were used, ranging from 1µs to 10 s. Each of the 256 NMR experiments consisted of 16 scans with a delay between the scans of 10 s. The delay between consecutive scans was needed to ensure complete recovery to thermodynamic equilibrium for even the longest possible relaxation times.

Results

Figure 4 shows a contour plot of the ^{1}H chemical shifts of the wide-line NMR spectrum of methane in the presence of the catalyst as a function of spin-lattice relaxation time. The data were obtained from the numerical algorithm applied independently to each chemical shift in the spectrum. Three different relaxation times are identified at 0.02-0.03 ms, 200-350 ms, and 600-750 ms. These are attributed to methane molecules adsorbed by the catalyst, methane molecules in the gas phase between the catalyst particles, and methane molecules in the gas phase above the catalyst filling in the sample container, respectively. The longest relaxation time, 600-750 ms compares favorably with the relaxation time of methane in the gas phase measured independently at the pressure of 23.8 atm without the catalyst. Because the contour plot doesn’t show a distinction between chemical shifts with respect to the different relaxation times, the chemical-shift axis doesn’t carry any added information. Therefore, the following experiments were conducted by showing data only on the relaxation-time axis.

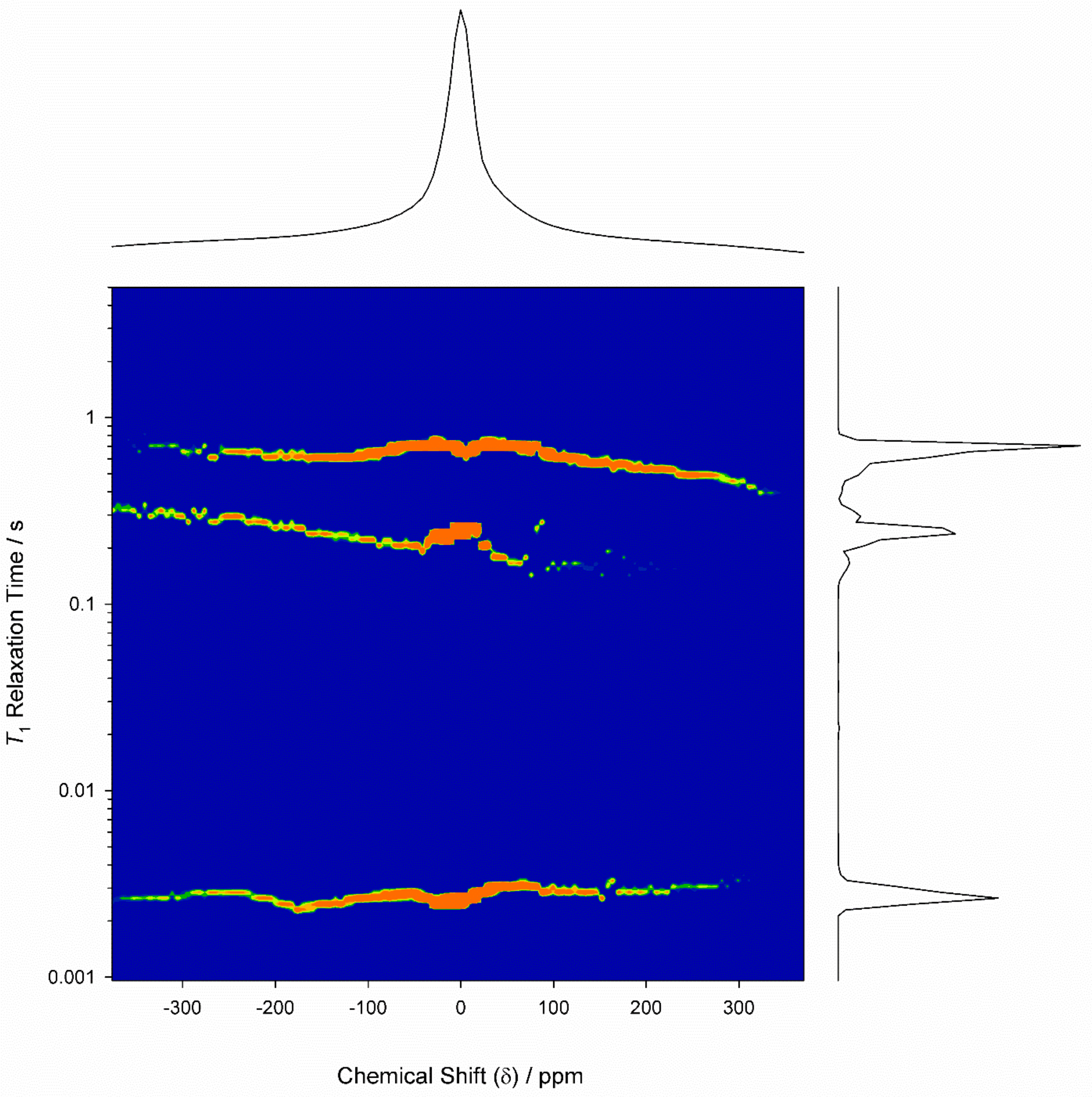

Figure 4: Contour plot of the wide-line chemical shift data of methane in the presence of the Cu-ZnO/Al_2O_3 catalyst at 23.8 atm as a function of spin-lattice relaxation times. Three different relaxation times can be seen (horizontal features) in the contour plot at 0.02-0.03 ms, 200-350 ms, and 600-750 ms. These are identified with methane molecules adsorbed by the catalyst, methane molecules in the gas phase between catalyst particles, and methane molecules in the gas phase above the catalyst filling, respectively. The spectrum on top of the contour plot is the projection of the chemical-shift data in the vertical direction; the plot to the right is the projection of the relaxation-time data in the horizontal direction.

The results of the numerical algorithm applied to a further-refined experimental series is shown in the plots of Fig. 5. The large plot shows the integrated intensities over the entire chemical shift-range (750 ppm) as a function of relaxation times. The smaller inset plot indicates five prevalent relaxation times at 0.0031 ms, 0.045 ms, 0.275 ms, 210 ms, and 650 ms. While the larger relaxation times are easily identified as before to be methane in the gas phase above (650 ms) and between (210 ms) the catalyst particles, the shorter relaxation times likely refer to differently adsorbed methane molecules. Because the catalyst consists of three different components (CuO, ZnO and Al_2O_3), it is tempting to identify each signal with methane adsorbed at each of the three catalyst components. However, further investigations are needed to confirm such speculation.

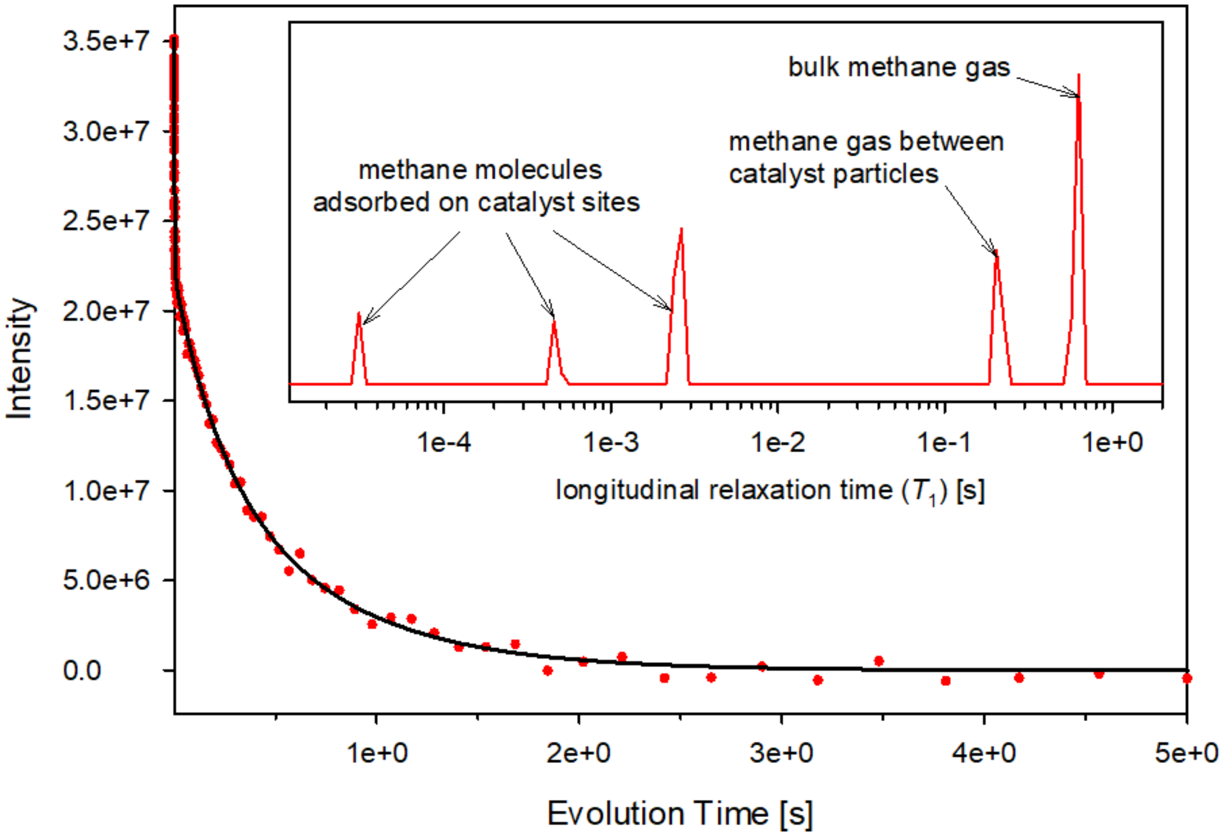

Figure 5: 1H-NMR signal intensities as a function of recovery time (evolution time) as measured by a modified inversion-recovery NMR experiment. The inset plot shows the spin-lattice relaxation times obtained from the inversion-recovery data by using the numerical algorithm. The five signals in the relaxation-time plot are identified with five different environments found for methane molecules.

Conclusion

This project was aimed at providing preliminary data for an investigation of the industrial methanol synthesis with NMR relaxometry. It provided a feasibility study of NMR relaxometry for gaseous compounds in the presence of a catalyst produced by one of the largest chemical companies (BASF) and used in their actual methanol production. The study showed different techniques to resolve relaxation times from inversion-recovery experiments. The contour plot representation did not provide additional information over a one-dimensional representation of the relaxation data. By refining the experimental conditions, up to five different relaxation times were resolved, which indicate the presence of methane in the gas phase as well as methane adsorbed at different sites of the catalyst. The results of this study are expected to assist further investigations and future experiments into the interactions between gaseous molecules and the $Cu\text{-}ZnO/Al_2O_3$ catalyst that is used in the industrial methanol synthesis. The technique will be expanded to investigate the interactions of other gases with the catalyst such as hydrogen and water vapor, or mixtures of gases. To emulate industrial conditions, measurements at elevated temperatures are also needed. Goal of the relaxometry studies will be to identify yield-inhibiting processes such as suspected water deposition on catalytically active sites.

Nomenclature

NMR (Nuclear Magnetic Resonance)

BASF catalyst (Cu-ZnO/Al_2O_3)

Methanol (CH_3OH)

Methane (CH_4)

Syngas gas ($CO + H_2$)

Water (H_2O)

Acknowledgements

I would like to thank Dr. Klaus Woelk for being my research advisor and for teaching me everything I know about R&D. I’d also like to thank Dr. Woelk’s research team for inspiring and helping me through this whole process. Lastly, thank you to the Opportunities for Undergraduate Research Experiences for giving me this opportunity.

References

[1] de Silva, M. J. (2016). Synthesis of Methanol from Methane: Challenges and Advances on the Multi-step (Syngas) and One-step Routes (DMTM). *Fuel Processing Technology* **145**, 42-61.

[2] Klerk, A. (2020). Transport Fuel: Biomass-, Coal-, Gas- and Waste-to-Liquids Processes *in* Future Energy (3rd Ed), Chapter 10, 199-226.

[3] Yang, L., & Ge, X. (2016). Biogas and Syngas Upgrading. *in* Advances in Bioenergy, Vol. 1, Chapter 3, 125-188.

[4] Woelk, K., Rathke, J. W., & Klingler, R. J. (1994). The Toroid Cavity NMR Detector. *J. Magn. Reason. Series A* **109**, 137-146.

[5] Jameson, C. J., Jameson, A. K., Smith, N. C., Hwang, J. K., & Zia, T. (1991). 13C and 1H Spin Relaxation in CH4 in the Gas Phase. *J. Phys. Chem.* **95**, 1092-1098.