Investigating Industrial Methanol Production with NMR

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Abstract

The compound Cu-ZnO/Al$_2$O$_3$ is used as catalyst for the industrial conversion of natural gas to the solvent methanol, even though its effectiveness is smaller than predicted by theory. Nuclear Magnetic Resonance (NMR) spectroscopy and relaxometry in toroid-cavity pressure probes is used to elucidate interactions of 10% hydrogen (H$_2$) and 90% nitrogen (N$_2$) gas mixtures with the active sites of Cu-ZnO/Al$_2$O$_3$. Toroid-cavity probes are special NMR probes built to record data in situ and at the high-temperature and pressure conditions of industrial processes. The spectroscopy data are analyzed using Langmuir adsorption theory for gas molecules on solid surfaces, while relaxometry data are evaluated by iterative refinement algorithms for extracting relaxation coefficients. While the relaxation data are inconclusive and don't provide new insight into interactions between H$_2$ and the catalyst, spectroscopy data point to pressure-dependent adsorptions of H$_2$ molecules on the catalyst's active sites.

Introduction

Methanol (CH$_3$OH) is an important raw material and precursor chemical for industrial and laboratory processes. It is commonly produced industrially by the syngas route that converts methane from natural gas through steam reforming into a mixture of carbon monoxide (CO), hydrogen gas (H$_2$), and water vapor (H$_2$O). This mixture is then converted further to methanol, which is an exothermic reaction but comes at the expense of an unfavorable, negative entropy balance. The syngas-to-methanol conversion is facilitated at the active sites of the solid catalyst Cu-ZnO/Al$_2$O$_3$ which yields only 7% of the desired product methanol in a single turnover reaction. However, theoretical calculations based on thermodynamic data suggest that the conversion should be as effective as 55%. There are other methods available for producing methanol that have higher conversion rates; however, these methods are currently too expensive to be considered economically attractive as a large-scale industrial option [1]. Previous research pertaining to the syngas method of methane-to-methanol conversion included Nuclear Magnetic Resonance (NMR) investigations were aimed at elucidating interactions of methane gas with the active sites of the Cu-ZnO/Al$_2$O$_3$ catalyst. Those investigations, however, were inconclusive due to the paramagnetic nature of the catalyst, which prevents the observation of high-resolution NMR-spectroscopic data. In this research project, NMR spectroscopy and NMR relaxometry with a toroid-cavity NMR pressure probe was conducted and used to study interactions of hydrogen gas molecules with the active sites of the Cu-ZnO/Al$_2$O$_3$ catalyst.

The results of the NMR investigations were analyzed using the Langmuir theory that describes the adsorption of gas molecules on a solid surface. In 1916 to 1918, Irving Langmuir first proposed an adsorption theory that is based on an equilibrium between molecules in the gas phase and those adsorbed on the surface. His theory is known as the Langmuir isotherm approach and was awarded with the 1932 Nobel Prize in chemistry [2]. Langmuir hypothesized that a surface has a defined number of equivalent sites to which gas molecules can be adsorbed by weak interactions. Langmuir's theory contradicted the then common approach that gaseous molecules would elastically

bounce off solid surfaces, and he replaced it with a model that included, and is based on, interactions between gaseous molecules and active surface sites [2].

Main Body

Method

The materials used throughout this investigation were a powdered Cu-ZnO/Al$_2$O$_3$ catalyst obtained originally from the chemical company BASF (Ludwigshafen, Germany) in the form of small pill-shaped pellets, as well as a gas mixture of 10% H$_2$ and 90% N$_2$. The gas mixture and its interactions with the Cu-ZnO/Al$_2$O$_3$ catalyst were analyzed using standard ^{1}H NMR spectroscopy and newly developed ^{1}H NMR relaxometry method. A specialized toroid-cavity NMR resonator, shown here in Fig. 1, was used as the NMR probe. The toroid-cavity probe is built to contain the sample inside a non-magnetic, cylindrical pressure vessel that is simultaneously used as NMR resonator [3]. With this specialized probe, in situ NMR spectroscopy can be conducted at pressures up to 200 atm and temperatures up to 250 °C. The toroid-cavity probe is fabricated from diamagnetic phosphor bronze with an inner hollow central conductor made from a copper-beryllium alloy. The central conductor is used to apply radio-frequency pulses to the sample under investigation and record NMR spectra while also being able to insert gaseous components into the vessel and monitor the applied gas

Figure 1: Toroid Cavity NMR Probe; image obtained from ref [3].

pressure. The toroid-cavity probe also contains a heating jacket around the pressure vessel and a thermocouple wire inserted from the bottom [3]. These two additional components provide accurate temperature control and monitoring.

The Cu-ZnO/Al$_2$O$_3$ catalyst pellets of BASF were ground up with a pestle in a ceramic mortar, which resulted in a fine powder (Fig. 2). The powder was then compacted into the toroid-cavity NMR pressure vessel (Fig. 3). The exact amount of catalyst utilized for each investigation was not recorded, because the Langmuir analysis for observing interactions between gaseous molecules and the active sites of a surface only requires pressure-dependent data that are relative to each other.
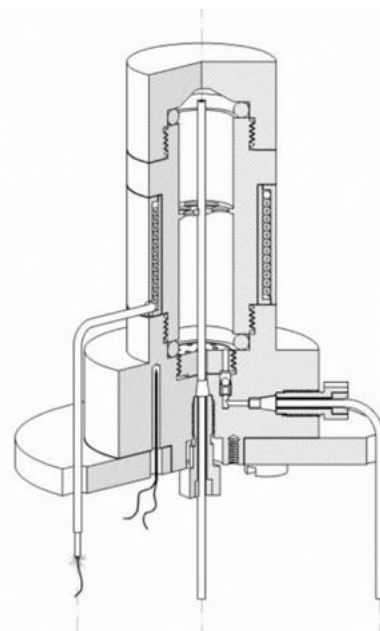
Figure 2: Procedure to obtain the Cu-ZnO/Al$_2$O$_3$ catalyst in powdered form.

Figure 3: Toroid-cavity Probe

Figure 4: View from the top into the toroid-cavity pressure vessel filled with powdered catalyst

Results

The first sets of data collected were from ^{1}H NMR spin-lattice relaxation experiments in a 200-MHz wide-bore Bruker Avance DRX NMR spectrometer. In total, there were 256 NMR spectra obtained in a series of experiment where each spectrum was recorded with 128 accumulated scans to reduce the spectral signal-to-noise ratio. The individual experiments were carried out with an initial radiofrequency-pulse excitation, after which NMR spectra were obtained using different recovery times. By varying the recovery time, a series of NMR spectra resulted where the signal intensities are functions of the recovery time. The recovery-time-dependent signal intensities were evaluated with a computational algorithm that reveals relaxation rates (R_1) or, equivalently, relaxation time constants ($T_1 = 1/R_1$) for the material under investigations. The series of experiments was then carried out several times with increasing pressures. While different relaxation time constants were expected for hydrogen molecules in the gas phase and for those adsorbed at the active sites of the catalyst, only a single relaxation coefficient could be extracted in each of these experiments. Because no distinction could be made between hydrogen gas molecules in their different environments (either in the gas phase or adsorbed), the NMR relaxometry investigations were inconclusive and did not contribute to a further understanding of the mechanisms of industrial methane-to-methanol conversions. Instead, the NMR signal intensities were evaluated directly as a function of hydrogen gas pressure, and a nonlinear relationship was detected. This nonlinear relationship was in contrast from the strictly linear relationship expected for an ideal gas, and it alluded to either the gas mixture behaving nonideal, or to a specific interaction between hydrogen molecules and the catalyst surface. This observation led to the series of new experimentations described in the following.

First, an NMR investigation was conducted with the 10% H_2 and 90% N_2 gas mixture but without the catalyst present. The results of this investigation were supposed to provide baseline data that would confirm the ideal-gas behavior of the gas mixture when no catalyst surface is available. The toroid-cavity NMR probe was emptied of the catalyst and cleaned by blowing out remaining catalyst particles completely with pressurized air. The toroid-cavity NMR probe was then inserted back into the spectrometer and pressurized with the gas mixture in a series of 41 individual NMR experiments. The pressure was incrementally increased starting at 0 atm and ending at 82 atm. Each spectrum was taken using 128 accumulated scans to increase the signal-to-noise ratio of spectral data. The 128 accumulated scans were preceded by 16 dummy scans that equilibrate the NMR recording conditions in the NMR probe. Dummy scans are scans taken under the same conditions that are applied with the regular scans, but without actually recording the data.
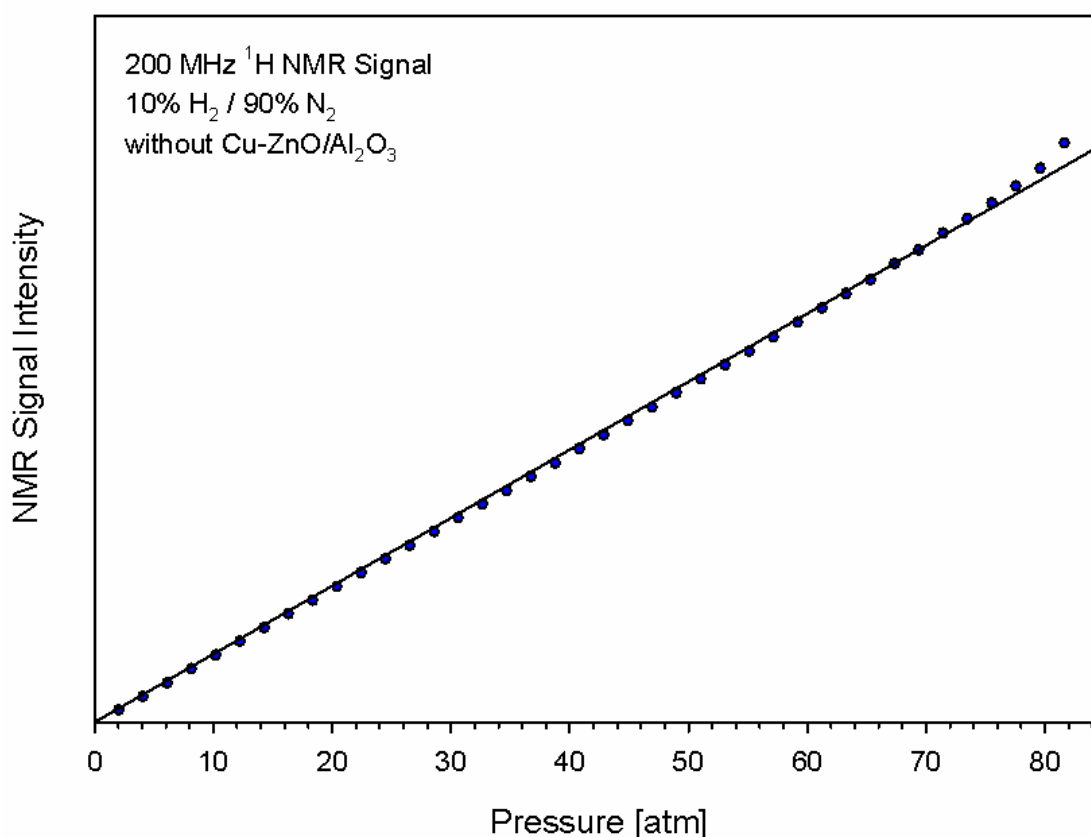

Figure 5: 200-MHz ^{1}H NMR signal intensities of the 10% H_2 and 90% N_2 gas mixture without the presence of the Cu-ZnO/Al$_2$O$_3$ catalyst as a function of pressure.

Figure 5 shows the NMR signal intensities obtained from the 10% H_2 and 90% N_2 gas mixture in the series of the 41 experiments with the pressure incrementally increasing from 0 atm to 82 atm but without the catalyst present. The plotted intensities provide a linear relationship between signal intensities and pressure, which confirms that the 10% H_2 and 90% N_2 gas mixture behaves as an ideal gas when no catalyst is present. Put

another way, the ¹H NMR signal intensity, which is directly proportional to the number of ¹H nuclei in the sample, is proportional to the pressure. This behavior is a confirmation of Avogadro's law that states that, at constant temperature and volume, the pressure of an ideal gas should be proportional to the pressure. This set of data was later used to show that the non-ideal behavior was due to interaction between gas molecules and catalyst, but not because of non-ideality within the gas phase.

Figure 6 shows the NMR spectrum of the 10% H_2 and 90% N_2 gas mixture in the presence of the with the Cu-ZnO/Al$_2$O$_3$ catalyst. Because the toroid-cavity NMR probe already showed substantial ¹H NMR signals even without a sample under investigation, which stem from nonmetallic, hydrogen-containing materials in the probe, such as Vespel® pressure seals, the spectrum in Fig. 6 is presented as the difference spectrum between the data recorded with the gas mixture and without. The catalyst was present in both the recording with the gas mixture and the recording without the gas mixture. This way, NMR signals that would originate from impurities in the catalyst were also eliminated. Accordingly, the difference between the baseline spectral data and the spectral data from the sample under gas pressure resulted only from signals of the 10% H_2 and 90% N_2 gas mixture. This difference spectroscopy was applied for all experiments reported in the following.

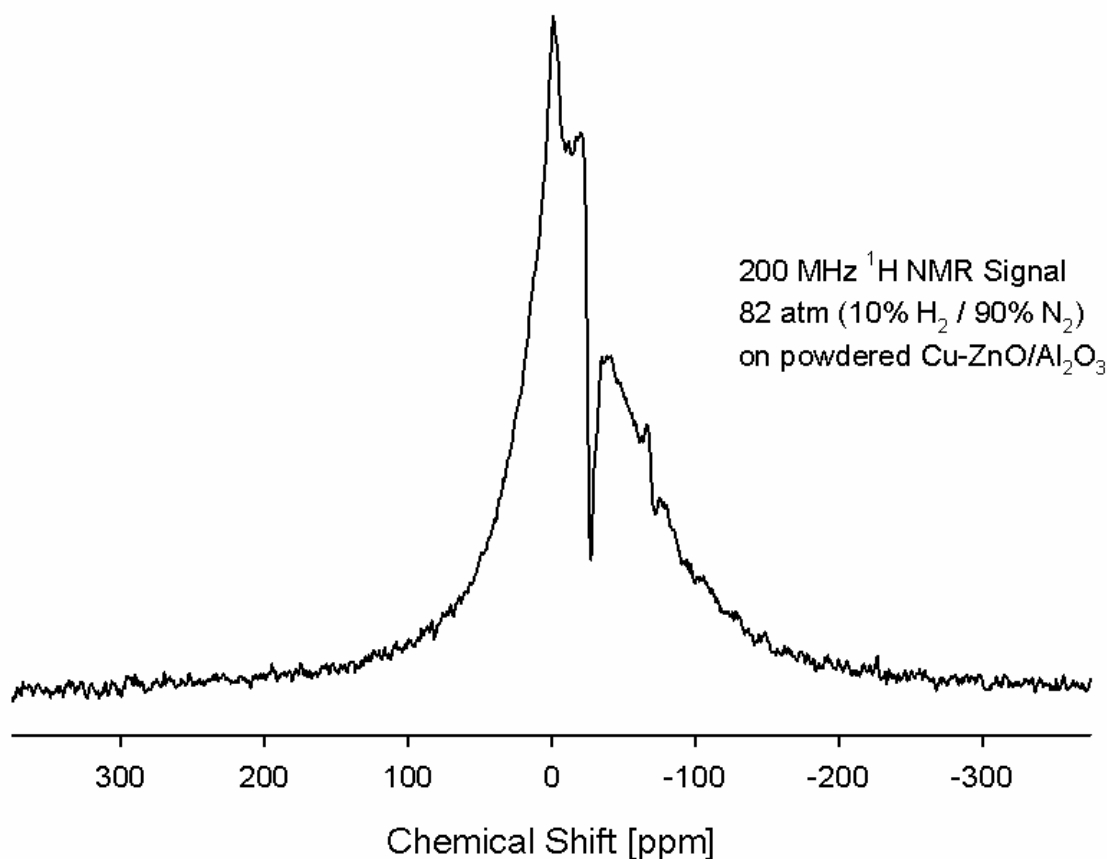Figure 6: 200-MHz ¹H NMR spectrum of the 10% H_2 and 90% N_2 gas mixture (82 atm) in the presence of the Cu-ZnO/Al$_2$O$_3$ catalyst.

Figure 7 shows NMR signal intensities of 41 experiments, where the 10% H_2 and 90% N_2 gas mixture is applied to the toroid-cavity NMR probe in the presence of the Cu-ZnO/Al$_2$O$_3$ catalyst as a function of gas pressure. The experimental data were fitted to the equation

$$S = aP + b\frac{KP}{1+KP}$$
Eq. (1)

where S is the NMR signal intensity, P is the gas pressure, K is the Langmuir constant, a is a scaling factor for the signal-intensity contribution from H_2 in the gas phase and b is a scaling factor for the contribution from surface-adsorbed H_2 [2]. As such, Equation (1) is a combination (addition) of the signal from the gas phase (scaled by the factor a) and the signal from the adsorbed species according to the Langmuir adsorption approach (scaled by the factor b). The contribution from the gas phase is considered linear with pressure, i.e., represented by aP in Eq. (1), due to the earlier analysis of the gas mixture that indicated that it is behaving as an ideal gas (Fig. 5). The contribution from the adsorbed material follows the Langmuir theory of single molecule adsorption per active site [2].
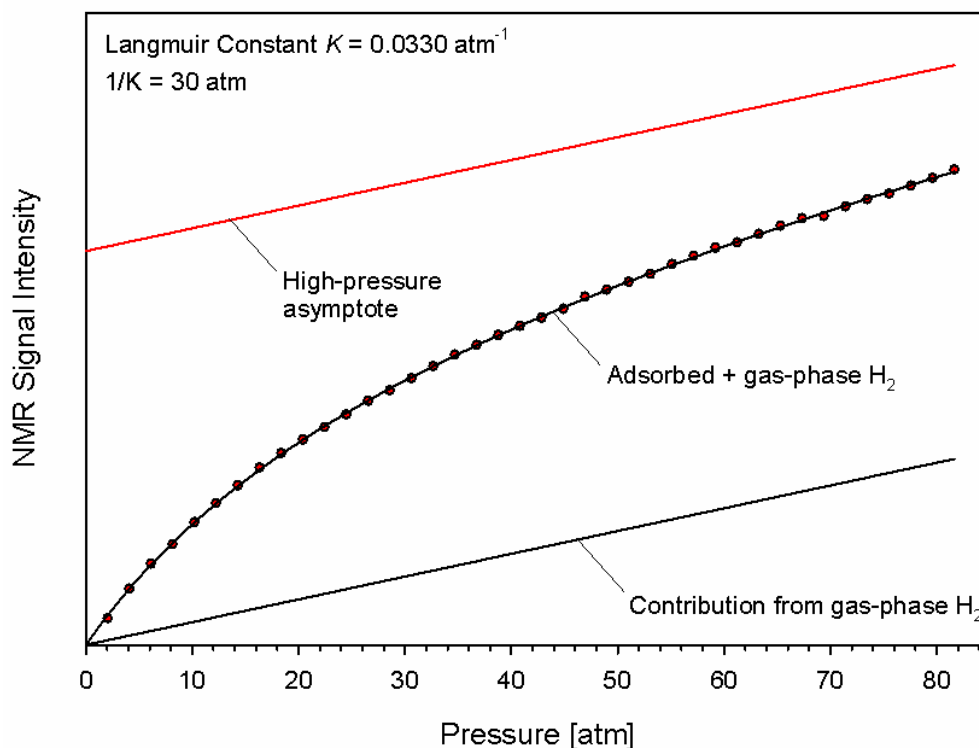

Figure 7: Signal Intensities of the 10% H_2 and 90% N_2 gas mixture in the presence of the Cu-ZnO/Al$_2$O$_3$ catalyst as a function of gas pressure. The straight lines represent the signal contribution from the gas phase (black line) and the high-pressure asymptote (red line) of complete occupation of all active sites at the catalyst. The line through the experimentally derived data (filled circles) was obtained from a curve fit of Eq. (1) by refining the Langmuir constant K and the scaling factors a and b as dependent parameters.

The inverse of the Langmuir constant, $1/K$ (as noted in Fig. 7), is known as the pressure at which one half of the active sites are occupied with adsorbate. From the optimization of Eq. (1) to fit the experimental data, the $1/K$ parameter was identified as 30 atm of gas pressure. However, in this case, the adsorbate may not only be H_2, but must be considered originating from the 10% H_2 and 90% N_2 gas mixture. Thus, the active sites of the catalyst can be occupied by either H_2 or N_2 molecules. The high-pressure asymptote indicates the line that is reached at very high pressures, i.e., when the pressure is so high that all active sites at the catalyst are filled with molecules from the 10% H_2 and 90% N_2 gas mixture.

Figure 8 shows NMR signal intensities of 41 experiments that were obtained in a similar way as in Fig. 7; however, the pressure experiment was conducted by first measuring the highest gas pressure (82 atm) and then incrementally decreasing the pressure to 0 atm. The same mechanism to fit Eq (1) to the experimental data was used refining the Langmuir constant and the scaling factors. The fact that the fitting procedure of the data in Fig. 7 and Fig. 8 results in different Langmuir constants may originate from a poor fitting of the data with large dependencies of the scaling factors on the Langmuir constant. It means that, to obtain a better fit, pressures higher than 82 atm must be investigated, or the percentage of hydrogen gas in the H_2/N_2 gas mixture must be increased in favor of H_2. Another explanation could be that the rate of adsorption (increasing pressure) is different from the rate of desorption (decreasing pressure).
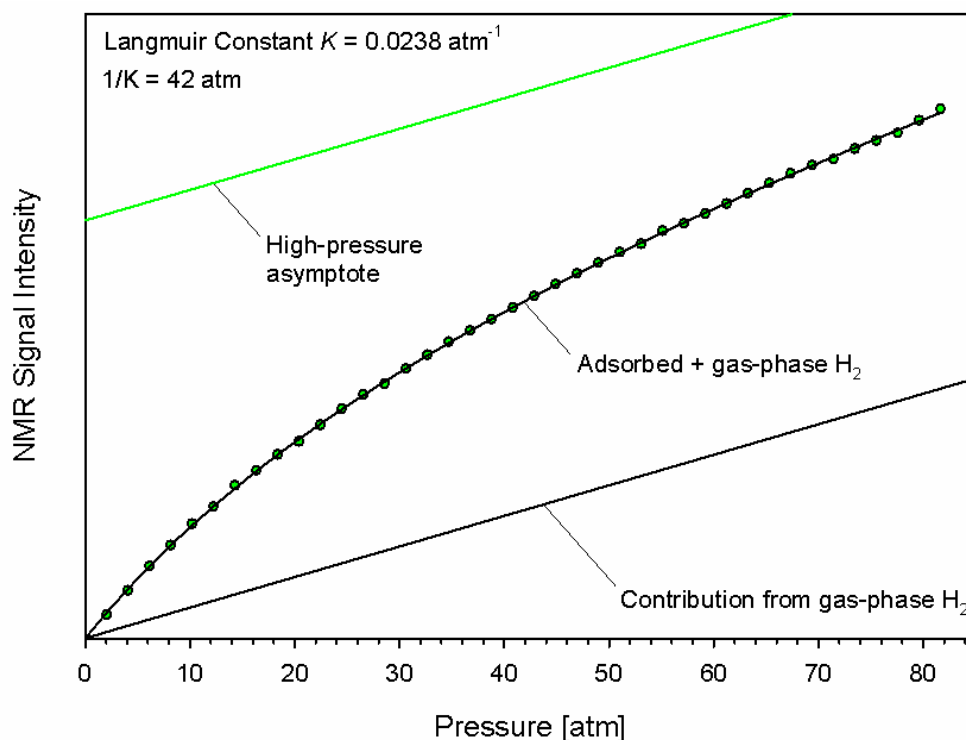

Figure 8: Signal Intensities of the 10% H_2 and 90% N_2 gas mixture in the presence of the Cu-ZnO/Al_2O_3 catalyst as a function of gas pressure. Similar to Fig. 7, the straight lines represent the signal contribution from the gas phase (black line) and the high-pressure asymptote (red line) of complete occupation of all active sites at the catalyst.

Considering that the gas mixture used in this study contained only 10% H_2, it could be speculated that the inverse Langmuir constant for pure hydrogen gas (100% H_2) would be somewhere between $1/K$ = 3 atm and $1/K$ = 4.2 atm. However, N_2 could block some of the active sites of the catalyst, which would mean that the inverse Langmuir constant would be lower than 1/10 of what was measured if only H_2 was present.

Discussion and Conclusion

This paper reports on results of NMR investigations with 10% H_2 and 90% N_2 gas samples applied to a Cu-ZnO/Al_2O_3 catalyst that is typically used in the large-scale industrial synthesis of methanol from natural gas. In this research project, NMR spectroscopy with a toroid-cavity pressure probe was used to study interactions of H_2 molecules with the active sites of the Cu-ZnO/Al_2O_3 catalyst. In a first series of experiments, it was found that NMR relaxometry was unable to distinguish between H_2 molecules in the gas phase and H_2 molecules adsorbed on active sites of the catalyst. The results were inconclusive and could not prove, nor deny, that considerable interactions exist between the gas molecules and the catalyst. However, the NMR relaxometry results pointed the project into a new direction, which led to using NMR spectroscopy results instead of relaxometry results. NMR spectroscopy experiments with the gas mixture and the catalyst, when fitted to the classical Langmuir approach of single site gas adsorption at a surface, were able to identify molecule adsorption on catalyst sites and even semi-quantify the strength of interaction between H_2 molecules and catalyst. To prove the ideal behavior of molecules in the gas phase up to 82 atm, control experiments in a high-pressure toroid-cavity NMR probe were needed without the catalyst present. Follow-up investigation with incrementally increasing and incrementally decreasing gas pressure from 0 atm to 82 atm and 82 atm to 0 atm, respectively, in the presence of the catalyst showed a non-linear relationship between NMR signal intensities and the gas pressure. The experimental data could be fitted to a theoretical approach that considered both the molecules in the gas phase, which followed the ideal gas law, and a single-site adsorption curve, which followed the Langmuir isotherm theory. The inverse Langmuir constant, which determines the pressure at which half the active sites are occupied with adsorbate was determined to be somewhere between $1/K$ = 3 atm and $1/K$ = 4.2 atm. However, N_2 molecules that are also present in the gas mixture may block some of the active sites of the catalyst, which would mean that the inverse Langmuir constant would be lower than calculated. Future investigations are needed to provide further insights into the occupation of active sites at the Cu-ZnO/Al_2O_3 catalyst including investigations in which higher gas pressures are applied. The investigations at higher pressures are expected to remove to some extent the dependency of the fitted parameter on each other and provide more certainty and consistency regarding the inverse Langmuir constant. Alternatively, gas mixture with a higher percentage of H_2 molecules should be used in the investigations.

Acknowledgements

References

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[2] Swenson, H., & Stadie, P. N., Langmuir's Theory of Adsorption: A Centennial Review, *Langmuir* (2019) *35*, 5409–5426.

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

Reflection on the Learning Experience

1. Describe your foundational understanding of how research is conducted in your discipline.
    a. Research is conducted in chemistry by trying thing based on a general understanding of the problem, and having most things tried not work. Most of research is redoing experiments and trying new things until you find a needle in a haystack.
2. How have you expanded your understanding of the informational resources available and how to best use these resources?
    a. I've discovered that the best informational resources available are the professors. They have a wealth of knowledge and all you have to do is ask. If they don't know the answers, then they will help you find them by either asking other professors or helping with a literature search.
3. Describe the knowledge you have gained regarding the fundamentals of experimental design.
    a. I have gained knowledge of experimental design by learning to follow the results instead of following an initial hypothesis to a dead end.
4. Describe how you have learned to interpret the results of your research.
    a. First of all, I have learned how to better interpret NMR spectra. I have also learned that you have to be open to things that you didn't expect to be in your results. For example, I expected my results to be in the form of relaxometry and not in a Langmuir adsorption curve.