

Final Report for Faculty Enhancement Grant: NMR of Modified Silica Gel

by Martha D. Bruch Spring, 2008

Due to a delay in processing of purchase orders, chemicals for preparation of modified silica gel samples were not obtained until July, 2007, which put the project behind the original schedule. Nonetheless, significant progress has been made, with completion of the project projected by the end of the summer of 2008. The results obtained thus far are summarized below; additional experiments are in progress.

The main objective of this project is to explore various synthetic approaches to attaching hydrocarbon chains to the surface of silica gel and to analyze the structure of the resultant surface. The chains attached to the surface form the basis for separation of mixtures using high pressure liquid chromatography (HPLC), and variation in the specific structures present has a dramatic effect on the performance of these materials in chromatographic columns. Increased performance is generally obtained when a highly cross-linked network of hydrocarbon chains is obtained on the silica surface. Extensive cross-linking reduces the number of unreacted hydroxyl groups on the silica surface, which makes the surface less susceptible to degradation over time when used to separate mixtures. This project seeks to obtain a better understanding of the relationship between the chain length of the hydrocarbon chain and the degree of cross-linking obtained on the surface. In addition, the effect of difunctional versus trifunctional ligands is also explored. It is anticipated that use of trifunctional ligands will lead to greater cross-linking.

A total of seven different modified silica gel samples have been prepared by my collaborator on this project, Dr. Hafeez Fatunmbi of Separations Method Technology in

Delaware. ^{29}Si CP/MAS NMR spectra have been obtained on all seven samples using the spectrometer at SUNY-ESF in Syracuse. The performance of the spectrometer was excellent, with high quality spectra obtained in three hours per sample. The experimental conditions were similar to those used to give reliable quantitative results on similar samples analyzed in the past, so it is assumed that reliable quantitative estimates of the relative amounts of different structures present on the surface can be obtained from the integrated intensities of the NMR signals.

Four of the modified silica gel samples involved attaching trifunctional ligands with different chain lengths to the surface of the silica gel. ^{29}Si NMR spectra revealed that surfaces prepared using only short chains containing one carbon (C1) have a much higher surface coverage with more extensive cross-linking than those prepared using only long chains containing eighteen carbons (C18). There are approximately twice as many total chains on the silica surface when C1 is used compared to C18, and this is consistent with previous results. For surfaces prepared using a mixture of long chains (C18) and short chains (C1), the surface coverage depends strongly on the ratio of long to short chains used in the mixed phase preparation. The sample with 4:1 ratio of long to short chains has more chains attached to the surface than surfaces prepared exclusively with long chains, with greater cross-linking observed, but the coverage is significantly less than observed in surfaces made exclusively using short chains. However, the mixed phase sample prepared using a 1:1 ratio of long to short chains shows higher coverage than either of the single phase samples, with a significantly greater amount of cross-linking. This supports the expectation that the short chains are able to insert themselves between the long chains to form a highly cross-linked network on the surface, leading to

greater surface stability when used for chromatographic applications. These results also demonstrate that the ratio of long to short chains used in the reaction mixture has a dramatic effect on the surface coverage and degree of cross-linking.

The other three samples prepared involved difunctional ligands. A surface prepared exclusively from difunctional short chains is compared to surfaces prepared from a mixture of trifunctional long chains and difunctional short chains, with ratios of 4:1 and 1:1. Similar results to those for the trifunctional mixed phase surfaces are obtained. ^{29}Si spectra show that the mixed phase sample prepared with a 4:1 ratio of long to short chains has less coverage than the surface prepared exclusively with difunctional short chains, whereas the mixed phase sample with a 1:1 ratio has approximately the same coverage as for difunctional short chains alone. The cross-linking is greater for the mixed phase samples, with the most cross-linking observed for 4:1 ratio of long to short chains. The greater amount of cross-linking despite lower overall coverage is likely due to the greater amount of trifunctional versus difunctional ligands in the mixture since trifunctional ligands (long chains) are expected to lead to greater cross-linking than difunctional ligands (short chains).

The ^{29}Si spectra provide information about the number of chains attached to the surface, but ^{29}Si spectra do not allow long and short chains to be distinguished. The relative number of long and short chains actually attached to the surface can be obtained from ^{13}C CP/MAS NMR spectra and compared to the ratio in the reaction mixture. Unfortunately, unlike ^{29}Si CP/MAS experiments, where quantitative results can be obtained from one spectrum obtained with a single mixing time, quantitative results in ^{13}C experiments require acquisition of a series of spectra obtained with variable contact

times, followed by non-linear curve-fitting to the integrated intensities. Consequently, the variable contact time experiments required for ^{13}C are more time consuming, and this experiment has only been performed on one sample to date. It was surprisingly easy to get a spectrum with good signal-to-noise ratio, requiring less time per spectrum than anticipated. The quantitative data for this sample has not yet been analyzed.

Further experiments have been postponed until May when more time is available to devote to research. It is anticipated that variable contact time ^{13}C experiments will be performed on the remaining samples during the summer, depending upon availability of the spectrometer at ESF. Once data analysis is complete, a paper will be written and submitted for publication at a peer-reviewed journal. The results will be presented at QUEST, 2009.