Conference Proceedings QENS2006 © 2007 Materials Research Society

A Quasi-Elastic Neutron Scattering Study of the Dynamics of Alkane and Ether Molecules Tethered to the Surface of MCM-41

F.J. Kintzel, Jr.[1], K.W. Herwig[1], M.K. Kidder[2], P.F. Britt[2], A.C. Buchanan, III[2], A.L. Chaffee[3]
[1]Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.
[2]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.
[3]School of Chemistry, Monash University, Victoria, Australia.

ABSTRACT

The motion of 1,3-diphenylpropane (DPP, $\equiv$Si-O-$C_6H_4(CH_2)_3C_6H_5$) and phenethyl phenyl ether (PPE, $\equiv$Si-O-$C_6H_4(CH_2)_2OC_6H_5$ and $\equiv$Si-O-$C_6H_4O(CH_2)_2C_6H_5$) tethered to the interior pore surface of MCM-41 silica was investigated using quasi-elastic neutron scattering. Quasi-elastic scans over an energy range of ± 17 μeV were carried out at temperatures in the range 240-320 K using the High Flux Backscattering Spectrometer at the NIST Center for Neutron Research. Quasi-elastic data were fit with a single-Lorentzian and a delta function, convoluted with the instrument resolution. These results elicit the role temperature has on the motion of these molecules tethered within the pores and the interactions of the molecules with the pore walls.

INTRODUCTION

Organic molecular interactions and transformations at interfaces form the foundation of many significant scientific fields and technologies including catalysis, chemical separations, and chemical sensing [1-8]. It is critical to probe both the structure and dynamics of the organic-inorganic interface to understand the underlying relationships that control reaction kinetics, mechanisms, and product selectivities. Because of the many potential applications in these areas, mesoporous silicas (e.g. MCM-41) and their derivatives have been widely investigated [1-4]. MCM-41 has been functionalized using a silyl-ether linkage (Si-O-C_{aryl}) to the surface to prepare samples of surface-immobilized 1,3-diphenylpropane (DPP, $\equiv$Si-O-$C_6H_4(CH_2)_3C_6H_5$) and phenethyl phenyl ether (PPE; PPE-1, $\equiv$Si-O-$C_6H_4O(CH_2)_2C_6H_5$ and PPE-3, $\equiv$Si-O-$C_6H_4(CH_2)_2OC_6H_5$). Pyrolysis of these materials is being investigated to examine the impacts of pore confinement on the free-radical reaction pathways [9,10].

Pore confinement has been shown to affect both the pyrolysis rate and product selectivity for surface-immobilized DPP at 375°C [9]. Both the rate and product selectivity were found to increase compared with the reaction of DPP in fluid phases and attached to a non-porous silica (Cabosil). In addition, these alterations in reactivity were found to be magnified as the pore size of the mesoporous silica decreased. Weak interfacial interactions, such as van der Waals interactions and hydrogen bonding, are typically overlooked in high temperature reactions. However, our preliminary research on ether-containing molecules such as PPE suggests that interactions with the surface silanols can have a substantial impact on product selectivities.

In the present study, we have carried out elastic and quasi-elastic neutron scattering (QNS) experiments to study the dynamics of DPP and PPE attached to the surface of MCM-41 as a function of temperature. Two different isomers of PPE are studied to see if the location of the ether oxygen may play a role in its ability to hydrogen bond with the surface silanols. Elastic measurements were used to indicate the appropriate temperatures for performing the full quasi-elastic scans.

XPERIMENTAL DETAILS

Two batches of hexagonal mesoporous silica, MCM-41 (2.8 and 3.0 mean pore diameters), were ynthesized according to standard procedures [9,10]. Nitrogen BET isotherms and FTIR spectroscopy ere used to characterize these silicas. DPP and PPE molecules were attached at maximum grafting ensities by condensation of a phenolic precursor (each in the *para*- position, e.g. p-$HOC_6H_4(CH_2)_3C_6H_5$ or the DPP case) with the surface silanols. Surface coverages (mmol per g of derivatized silica) were etermined by a standard base hydrolysis method and also by carbon elemental analysis [9,10], which greed to ± 3 %, and the average values are given in the table below. DPP and PPE grafting densities, hich are normalized for the different surface areas and mass of organic, are also given in the table. The aximum grafting densities are similar for the three molecules as expected based on their similar size nd grafting position. Samples of the original underivatized MCM-41 silicas were retained for easurements of background. All samples were stored in sealed, evacuated glass ampoules.

Prior to loading the DPP/MCM-41 or PPE/MCM-41 samples into their respective sample cell, the ass of the sample cell and aluminum foil section was measured and recorded. The sample cell, foil, nd sample were then transferred to a helium-filled glove box. Each sample was removed from its acuum sealed glass container and evenly distributed onto the pre-cut section of aluminum foil. The foil ith sample was then carefully folded, sealed, formed into an annular ring, and placed within the sample ell such that the foil annulus was flush to the bottom and sides of the cell interior. The sample cell was en sealed with an indium o-ring and reweighed to determine sample mass. Under these conditions, 0.8 g of each DPP/MCM-41 and PPE/MCM-41 sample were placed into the beam confined as a thin nular ring between two sheets of aluminum foil placed into a standard 29 mm wide sample can (8 - 0% scatterer).

All measurements were carried out using the High Flux Backscattering Spectrometer (HFBS) cated at the NIST Center for Neutron Research (NCNR). The NCNR backscattering spectrometer ables high energy resolution studies of the low frequency dynamics of many systems. In addition to robing dynamics, HFBS can be operated with the Doppler monochromator at rest. This type of "fixed indow scan" is a useful technique to determine the conditions for which the dynamics of the system e within the dynamic range of the instrument.

At HFBS the incident neutron wavelength is varied via Doppler selection about a nominal value of .271 Å (E_0=2.08 meV). After scattering from the sample, only neutrons having a fixed final energy of .08 meV are measured by the detectors as ensured by Bragg reflection from analyzer crystals. The strument was operated with a dynamic range of ±17 μeV. With this dynamic range, the full width of e sample-dependent instrument resolution function at half maximum was 0.85 μeV.

The sealed sample cell was then mounted onto the cold stage of a closed-cycle refrigerator, which ontrols the sample temperature to within ±0.1 K. Initial measurements of the elastic intensity beginning a base temperature of 50 K and increasing at a rate of 1 K/min to 380 K were carried out. Quasi-astic scans were carried out within an energy transfer range of ±17 μeV on each sample in the mperature range 240 – 320 K. The data collected at eleven detectors (0.56 $Å^{-1}$ <Q <1.60 $Å^{-1}$ at the astic channel) have been used in the data analysis.

able 1: Surface Coverage Analysis for Organically Modified MCM-41.

Sample	MCM-41	Surface Coverage (mmol g^{-1})	Grafting Density (molecule nm^{-2})
Si-O-$C_6H_4(CH_2)_3C_6H_5$ (DPP)	**3.0 nm; 1047 m^2 g^{-1}**	**1.81**	**1.61**
Si-O-$C_6H_4O(CH_2)_2C_6H_5$ (PPE-1)	**2.8 nm; 913 m^2 g^{-1}**	**1.61**	**1.56**
Si-O-$C_6H_4(CH_2)_2OC_6H_5$ (PPE-3)	**2.8 nm; 913 m^2 g^{-1}**	**1.54**	**1.46**

DISCUSSION

Data from the quasi-elastic runs were reduced to the dynamic structure factor, S(Q,ω), using Data Analysis and Visualization Environment (DAVE) software [11] from the NIST Center for Neutron Research (NCNR). The reduced data were fit to the sum of a delta function (δ), single-Lorentzian (l), and linear background (b), convoluted with the measured instrument resolution. Δ and L are the integrated intensities of the δ and l components of the total scattered intensity, respectively. Δ was reduced by the measured elastic scattering from the MCM-41 substrate. At each sample temperature the elastic incoherent structure factor (EISF) defined as EISF = Δ/(Δ+L) was calculated for each Q in the range 0.56 $Å^{-1}$ < Q <1.60 $Å^{-1}$. The EISF represents contributions from the tethered molecules only.

The results of this analysis are represented in a series of curves displayed in Figure 1. The EISF of DPP, PPE-1, and PPE-3 at 240, 280, and 320 K have been plotted as a function of Q. At the lowest temperature, there is a decrease in the elastic intensity at each Q for PPE-3, PPE-1, and DPP molecules, respectively. Since the MCM-41 pore diameters and PPE and DPP grafting densities are similar for the samples, the observed EISF variations can be related to the presence and position of the oxygen atom in the tethered molecules. As indicated by the inset in Figure 1, the location of the oxygen atom for PPE-3 is farthest from the tether point to the surface compared to PPE-1. The smallest loss of elastic intensity was observed for the PPE-3 molecules indicating reduced mobility relative to both DPP and PPE-1. We attribute this to an increased probability of PPE-3 interacting with the MCM-41 pore surface due to the location of the oxygen atom along the propane linkage. In PPE-1, the oxygen atom is located closer to the tether point and the molecule geometry likely inhibits its interaction with the MCM-41 surface.

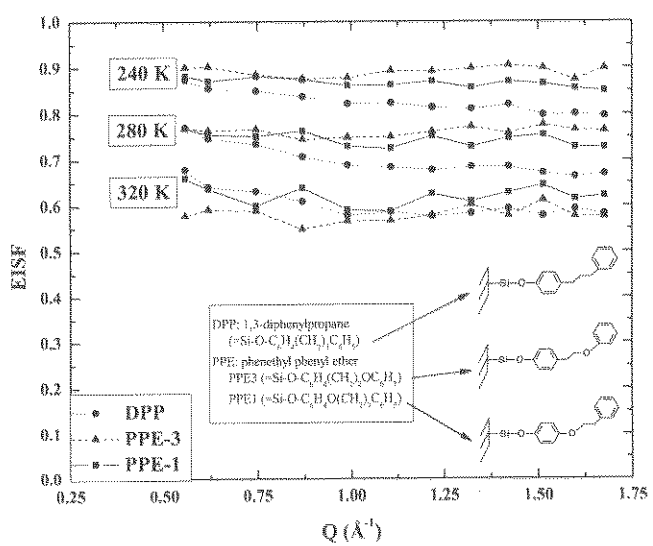
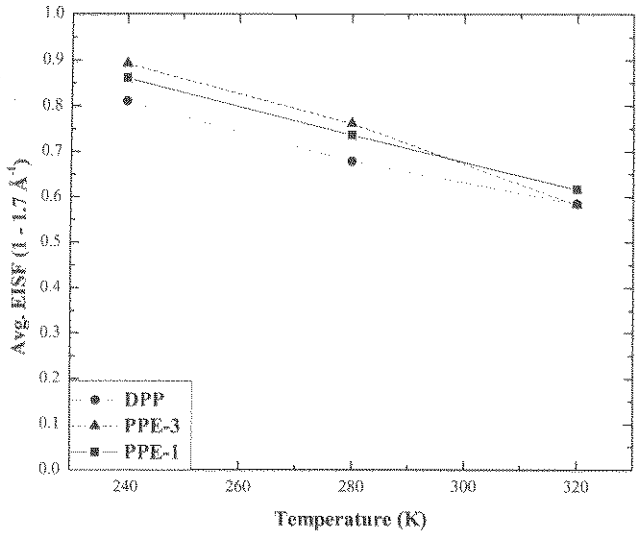


Figure 1: Temperature and Q-dependence of the EISF for DPP (circles and dotted lines), PPE-1 (squares and solid lines), and PPE-3 (triangles and dashed lines) tethered within the pores of MCM-41.



ure 2: EISF averaged over a Q-Range 1 – 1.7 Å^{-1} as a function of temperature for DPP (circles and ted lines), PPE-1 (squares and solid lines), and PPE-3 (triangles and dashed lines) tethered within the es of MCM-41.

This overall trend persists at a sample temperature of 280 K. Compared to the 240 K results, an roximate 15% decrease in average EISF values is observed for all tethered molecules (Figure 2). is further drop in elastic intensity at 280 K can be interpreted as an increase in the molecular mobility he pores. Raising the sample temperature to 320 K resulted in an additional drop in the EISF and an litional corresponding increase in the ability of the molecules to move within the MCM-41 pore. ile at 240 and 280 K there is evidence of the influence of the presence and location of oxygen along linkage, at 320 K this effect is not apparent. At this elevated temperature, the influence of the oxygen m apparently no longer plays a role in determining the fraction of mobile molecules.

In the present analysis, we assume the molecular motions can be described by a single relaxation e τ, and have the form of a Lorentzian lineshape with a full-width at half-maximum (FWHM) cribed by FWHM = $2\Gamma = 2\hbar/\tau$, where Γ is the half-width at half-maximum (HWHM). The perature dependence of the relaxation times for each tethered system is displayed in Figure 3. As ected, the DPP and PPE dynamics show an increase in relaxation times as the temperature of the tem decreases. There is a marked difference when comparing the relaxation times for DPP and PPE-1 hose found for the PPE-3 system. The relaxation times for DPP and PPE-1 are similar, increasing m ~210 ps to ~310 ps as temperature decreases. At all temperatures, the relaxation times for PPE-3 significantly longer then observed for either PPE-1 or DPP. The slower dynamics for PPE-3 at all peratures compared to PPE-1 demonstrates the effect of oxygen atom location and suggests that cement of the oxygen atom farther from the tether point allows enhanced interaction with surface nols via hydrogen bonding. The presence of oxygen in PPE-1 has only a minimal impact on the time

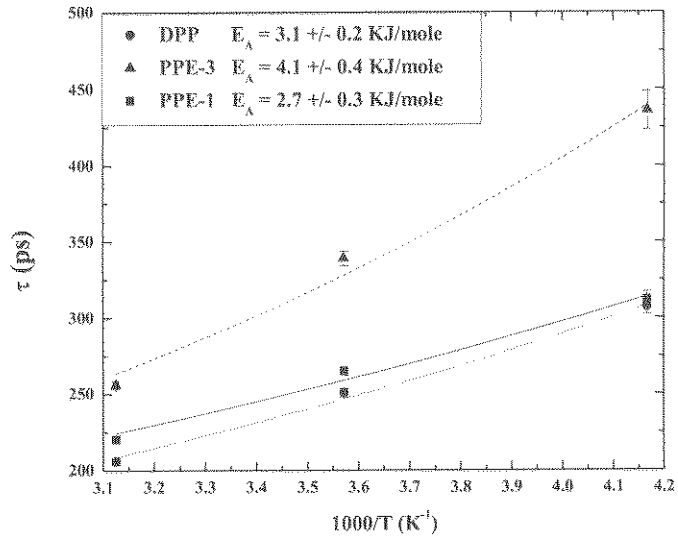


Figure 3: Temperature dependence of the relaxation times for DPP (circles), PPE-1(squares) and PPE-3 (triangles) tethered within MCM-41. Lines running through each plot represent an Arrhenius Law fit to each data set. Activation energies for each molecule, based on the fits, are indicated in the key to the upper left in the plot.

scale of the dynamics when compared with DPP, suggesting it is less accessible for hydrogen bonding interactions with the pore surface. The effectiveness of these interactions with the surface may depend on molecular grafting densities and MCM-41 pore sizes, and these parameters will be the subject of future investigations. Activation energies for each tethered system are calculated using the relaxation time data. The curve fits to the data demonstrate an Arrhenius Law behavior with activation energies $E_A = 3.1 \pm 0.2$, 2.7 ± 0.3, and 4.1 ± 0.4 KJ/mole for DPP, PPE-1, and PPE-3, respectively. The larger activation energy for PPE-3 compared with the other molecules is consistent with the interpretation of stronger interactions of this molecule with the pore surface.

CONCLUSIONS

The dynamics of 1,3-diphenylpropane (DPP, $\equiv$Si-O-$C_6H_4(CH_2)_3C_6H_5$) and phenethyl phenyl ether (PPE; PPE-1, $\equiv$Si-O-$C_6H_4O(CH_2)_2C_6H_5$ and PPE-3, $\equiv$Si-O-$C_6H_4(CH_2)_2OC_6H_5$) tethered to the interior pore surface of MCM-41 was investigated using quasi-elastic neutron scattering. The relationship between sample temperature and molecular motions within the pore yielded the following trends:

- Increasing the sample temperature resulted in a corresponding decrease in elastic intensity, indicating increased mobility of the molecules within the MCM-41 pore.

- The location of the oxygen along the linkage affected the dynamics within the pore. As the distance of the oxygen atom from the tether point increased, the probability of the oxygen to interact with the

MCM-41 surface increased. This effect is clearly observed when comparing relaxation times (τ) for PPE-3 and PPE-1, as τ was significantly larger in the PPE-3 system at all temperatures.

- The absence of oxygen along the propane linkage in DPP resulted in the largest loss in elastic intensity and correspondingly shortest relaxation times.

- An Arrhenius Law behavior was demonstrated for each system within the limited temperature range 240-320 K.

The results of these initial QNS measurements have provided the foundation for subsequent experiments. An additional QNS study is planned to study the effects that pore size, temperature, and grafting density have on the dynamics of both DPP and PPE tethered to MCM-41. A comparison of $S(Q,\omega)$ from experiment to those from a molecular dynamic simulations for a model of DPP and PPE grafted onto the surface of MCM-41 developed by Dr. A.L. Chaffee [12] will also be carried out.

ACKNOWLEDGEMENTS

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. ORNL/SNS is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725. This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0454672. We acknowledge the support of the National Institute of Standards and Technology, U. S. Department of Commerce, in providing the neutron research facilities used in this work.

REFERENCES

1. Thomas, J.M., Johnson, B.F.G., Raja, R., Sankar, G., Midgley, P.A., *Acc. Chem. Res.* **2003**, *36*, 20.
2. McKittrick, M.W., Jones, C.W., *J. Am. Chem. Soc.* **2004**, *126*, 3052.
3. Lee, B., Bao, L.-L., Im, H.-J., Dai, S., Hagaman, E.W., Lin, J.S. *Langmuir* **2003**, *19*, 4246.
4. Ueno, Y., Tate, A., Niwa, O., Zhou, H.-S., Yamada, T., Honma, I. *Chem. Commun.* **2004**, 746.
5. Turro, N.J. *Chem. Commun.* **2002**, 2279.
6. Rouhi, A.M. *Chem. Eng News* **2000**, *78 (Aug 21)*, 40.
7. Wang, J.-Y., Chen, W., Liu, A.-H., Lu, G., Zhang, J.-H., Yang, B.J. *J. Am. Chem. Soc.* **2002**, *124*, 13358.
8. Blomberg, S., Ostberg, S., Harth, E., Bosman, A.W., van Horn, B., Hawker, C.J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1309.
9. Kidder, M. K.; Britt, P. F.; Zhang, Z.; Dai, S.; Hagaman, E. W.; Buchanan, A. C. III *J. Am. Chem. Soc.* **2005**, *127*, 6353.
10. Kidder, M. K.; Britt, P. F.; Zhang, Z.; Dai, S.; Buchanan, A. C., III *Chem. Commun.* **2003**, 2804.
11. http://www.ncnr.nist.gov/dave
12. Chaffee, A. L. *Fuel Process. Technol.* **2005**, *86*, 1473.