

Behaviour of Mesoporous Silica (MCM-41) Supported Catalysts in Degradation Reactions

*C.P. Guthrie, **E.J. Reardon and ***H. Peemoeller

University of Waterloo, Waterloo, ON, Canada

*cpguthri@uwaterloo.ca, **ejreardon@uwaterloo.ca, ***peemoeller@uwaterloo.ca

ABSTRACT

A dissolution experiment indicated that Pd/MCM-41 is more stable in contact with deionized water at $25 \pm 0.1^\circ\text{C}$ than MCM-41 and the stability increased with increasing mass loading of Pd. A long term dissolution experiment showed that MCM-41 retained its characteristic hexagonal structure and high surface area after 1,174 days of contact with deionized water. Samples of Pd/MCM-41 absorbed 0.85 ± 0.18 moles of hydrogen per mole of Pd present in a series of experiments in pressure cells at $25 \pm 0.1^\circ\text{C}$ and approximately 101.3 kPa. Pd/MCM-41 exhibited substantial longevity while degrading at least 91% of inflow trichloroethylene (TCE) concentrations in hydrogen-saturated deionized water over 5,036 pore volumes during a column experiment. The dominant breakdown product of TCE degradation in the presence of Pd/MCM-41 was ethane. Minimal concentrations of intermediate degradation products were detected, suggesting that TCE degraded to ethane before desorbing from the Pd/MCM-41 surface.

Keywords: MCM-41, degradation, trichloroethylene, hydrogen, palladium

1 INTRODUCTION

Research was carried out to investigate several aspects of Mobil's composition of matter #41 (MCM-41) pertaining to its potential application in water treatment technologies. The envisaged technology is presented in Figure 1. The goal of the work was to lead to a recommendation of whether further work investigating this particular, potential application is warranted at the present time. This goal was approached by investigating the long-term stability of MCM-41 and MCM-41-supported metals in deionized water, quantifying the maximum absorption of hydrogen by Pd/MCM-41, and demonstrating the long term ability of Pd/MCM-41 to induce degradation of chlorinated volatile organic compounds such as trichloroethylene.

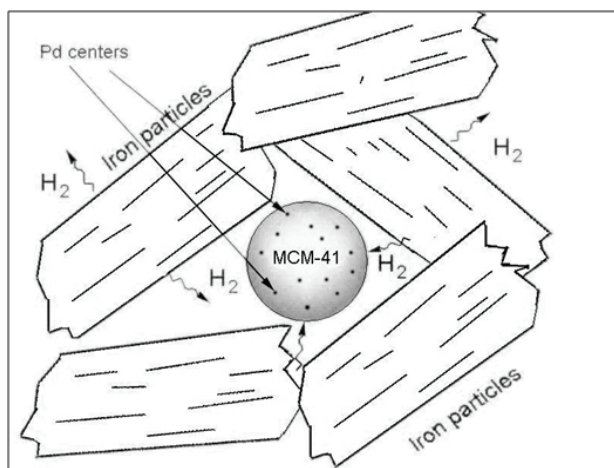


Figure 1: Representation of the Pd/MCM-41 and zero-valent iron technology (After Reardon, E. J. (2005) Presentation at the Waterloo/Dupont Iron Technology in Groundwater Remediation Meeting, Waterloo, 3-30-2005).

2 PREPARATION OF MATERIALS

MCM-41 was synthesized according to published procedures [1-3]. MCM-41 is formed via a liquid crystal template mechanism where silica tetrahedrons form around rod-like arrangements of organic surfactant micelles in a hexagonal arrangement [4,5]. Tetramethylammonium hydroxide (TMAOH) and cetyltrimethylammonium bromide (CTABr) were dissolved in Nanopure[®] deionized water under gentle stirring at 300 K. Fumed silica powder was added once the opaque solution turned clear and the resulting mixture was stirred and heated for 3 h. Final molar composition of the gel was 1 SiO₂, 0.19 TMAOH, 0.27 CTABr, 40 H₂O. Required masses of reagents were calculated on a basis of 250 g of water. The gel was covered with Parafilm[®] and aged for 24 h at room temperature. The gel was transferred to a stainless steel autoclave sealed with a Viton Teflon O-ring and heated for 68 h at 400 K. The reaction was arrested by quenching the autoclave under cold water for 0.5 h. Autoclave contents were transferred to plastic centrifuge bottles and washed, centrifuged, and decanted 12 times, or until the conductance of the supernatant rinsate was less than 10 $\mu\text{S}/\text{cm}$. The solid material was calcined under air for 8 h at 923 K to ensure complete removal of the organic template.

Palladized MCM-41 (Pd/MCM-41) was prepared following a published procedure [6]. The Pd source ($\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$) dissociates in solution, forming Pd^{2+} . Different mass percent loadings of Pd on MCM-41 were achieved by dissolving appropriate masses of the palladium source into small volumes of deionized water, which was added dropwise to dry MCM-41 following an incipient wetness technique [7]. Material was placed under vacuum for 30 min and dried overnight at 393 K. The vacuum treatment ensured Pd solution entered the pores of MCM-41. The material was then calcined under air for 3 h at 593 K. An SEM image of an as-synthesized Pd/MCM-41 sample is presented in Figure 2.

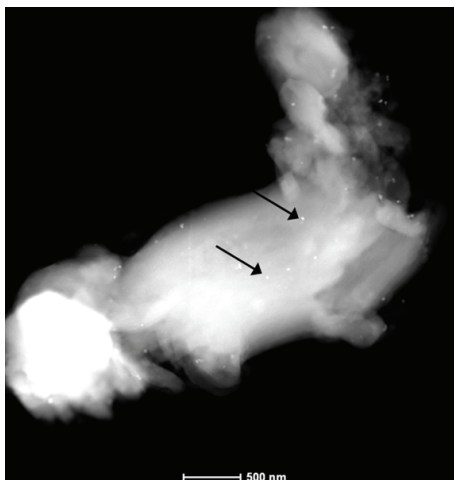


Figure 2: SEM image for Pd impregnated MCM-41 (0.12% Pd/MCM-41) showing the outline of an MCM-41 particle with Pd centres visible on its surface.

3 STABILITY OF MCM-41-SUPPORTED METAL AND LONG TERM STABILITY OF MCM-41

A dissolution experiment indicated that Pd/MCM-41 is more stable in contact with deionized water at $25 \pm 0.1^\circ\text{C}$ than purely siliceous MCM-41.

Stability increases with increasing mass percent loading of Pd in the Pd/MCM-41 material (Figure 3). Simulated results in Figure 3 were produced via Phreeqci by assuming a similar dissolution behaviour as quartz and adjusting for the enhanced surface area and dissolution rate of MCM-41. The increased stability was attributed to a reduction in Pd/MCM-41 surface areas relative to the parent MCM-41 material. The reduction in surface area is likely the result of partial or complete blocking of the MCM-41 mesopores by Pd centres.

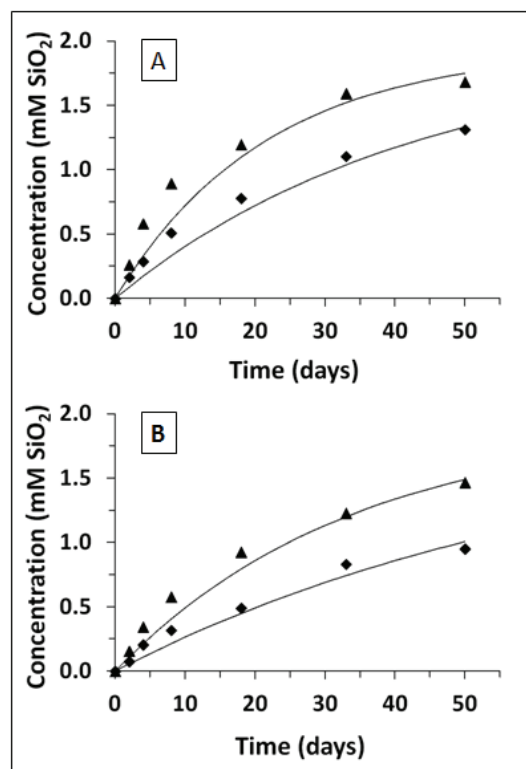


Figure 3: Comparison of simulated and experimental dissolution results for: (A) 0.12% Pd/MCM-41, and (B) 1.16% Pd/MCM-41. Experiment results are represented by \blacktriangle (solid/liquid = 1/100) and \blacklozenge (solid/liquid = 1/200). Lines represent results simulated using Phreeqci.

Ni/MCM-41 was less stable in contact with deionized water than MCM-41 and Pd/MCM-41. Both Ni and Pd impregnated MCM-41 exhibited enhanced stability relative to purely siliceous MCM-41 in 0.01 M NaCl solution (Figure 4). The stability enhancement was more pronounced for Pd/MCM-41.

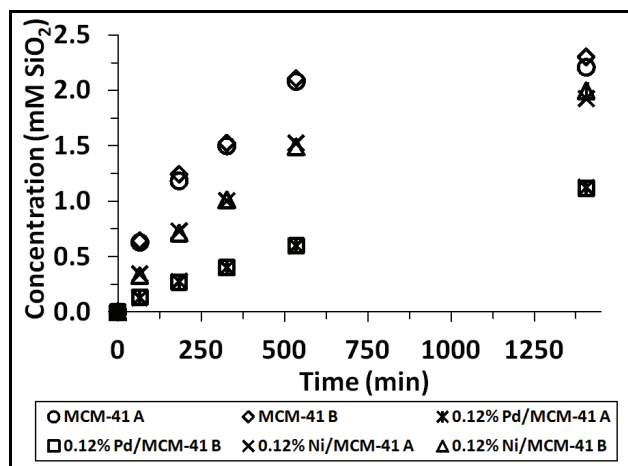


Figure 4: Results of dissolution experiments comparing purely siliceous MCM-41, 0.12% Pd/MCM-41, and 0.12% Ni/MCM-41 in a 0.01 M NaCl solution.

A long term dissolution experiment showed that MCM-41 retained its characteristic hexagonal mesopore structure and high surface area after 1,174 days of contact with deionized water (Figure 5). Peaks in Figure 5 are labelled according to the Miller indices of a hexagonal unit cell. Surface area analyses indicated a decrease from 874 m²/g to 841 m²/g after 1,174 d of contact with deionized water (4% decrease).

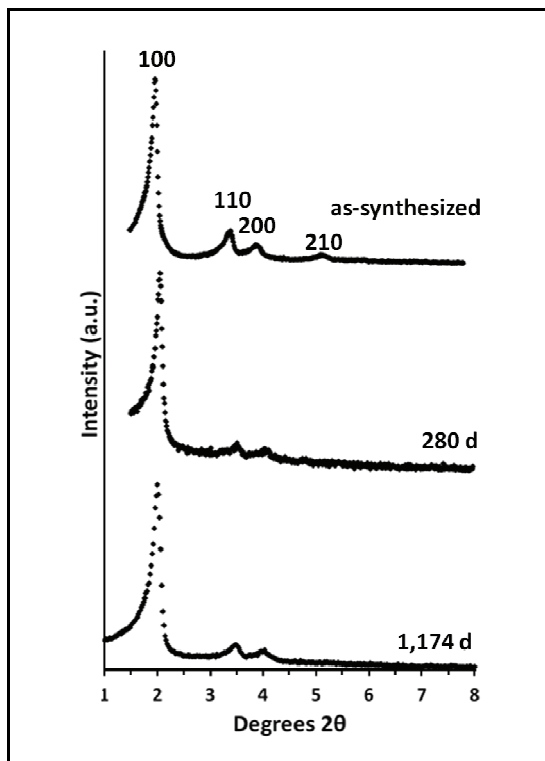


Figure 5: Comparative low angle XRD plots for as-synthesized MCM-41 as well as material recovered after 280 d and 1,174 d contact with deionized water.

4 HYDROGEN UPTAKE BY Pd/MCM-41

The ability of Pd/MCM-41 to absorb hydrogen was investigated in a series of experiments in pressure cells at 25±0.1°C and approximately 101.3 kPa. The Pd in Pd/MCM-41 was able to absorb 0.85±0.18 moles of hydrogen per mole of Pd present (Figure 6). This was a higher level of absorption than found in most other, published Pd-hydrogen investigations. It is proposed that enhanced uptake of hydrogen by Pd/MCM-41 may be the result of a higher proportion of surface and subsurface sites in the samples relative to other supported Pd materials.

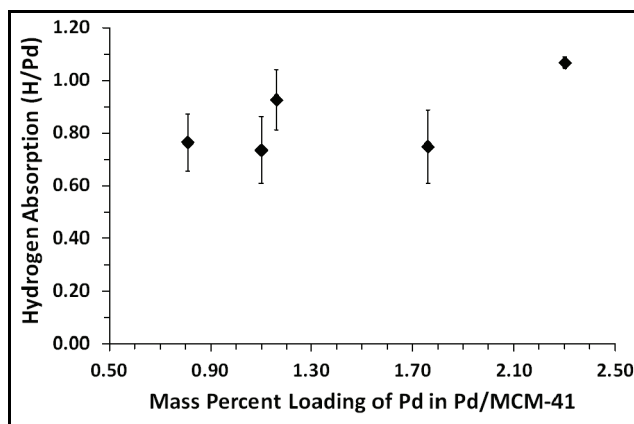


Figure 6: Results of hydrogen absorption by Pd/MCM-41 samples at different mass percent loadings of Pd.

5 DEGRADATION OF CONTAMINANTS BY METAL IMPREGNATED MCM-41

Column trichloroethylene (TCE) degradation experiments indicated that Pd/MCM-41 has substantial longevity while degrading at least 91% of inflow TCE concentrations in hydrogen-saturated deionized water over 5,036 pore volumes (Figure 7). The average inflow TCE concentration was $4.94 \times 10^{-2} \pm 4.87 \times 10^{-3}$ mmol/l with maximum and minimum concentrations of 7.24×10^{-2} mmol/l and 2.63×10^{-2} mmol/l, respectively. The dominant breakdown product of TCE degradation in the presence of Pd/MCM-41 was ethane. Minimal concentrations of intermediate degradation products were detected, if at all. This result suggests that TCE completely degrades to ethane before desorbing from the Pd/MCM-41 surface.

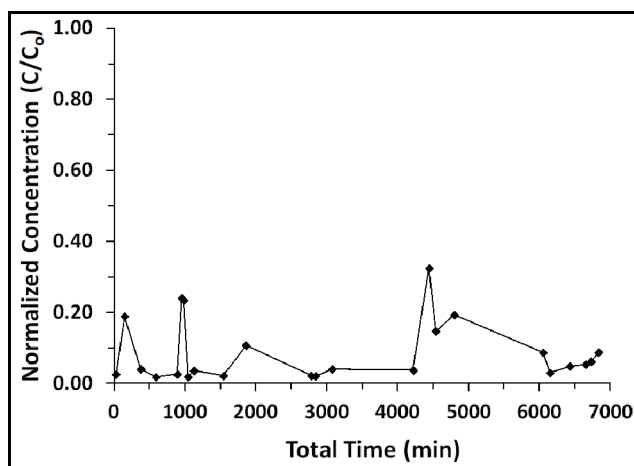


Figure 7: Long term normalized TCE concentration results versus total time for 0.99% Pd/MCM-41 column (5,036 pore volumes).

It was shown that Pd/MCM-41 was more effective and had better longevity at treating inflow TCE compared to a

lower cost substitute such as Pd/sand (Figure 8). Unlike Pd/MCM-41, Ni/MCM-41 did not induce degradation of TCE. Column experiments using Ni-Pd/MCM-41 materials indicated that while the material does induce degradation of TCE, the Pd cannot be substituted for Ni on a 1:1 basis while still obtaining similar degradation results as Pd/MCM-41.

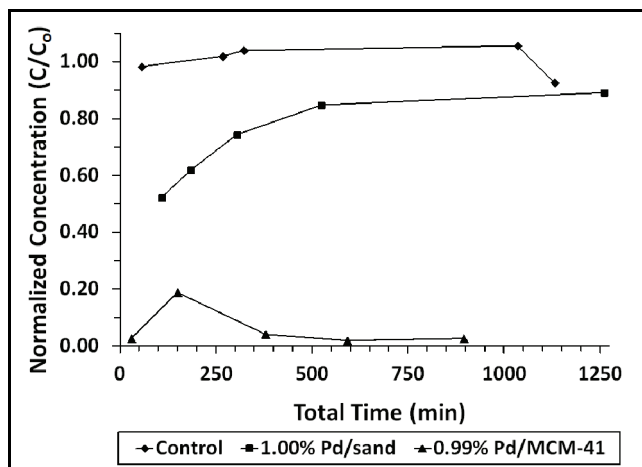


Figure 8: Results from TCE degradation columns including a non-reactive control sample, 1.00% Pd/sand, and 0.99% Pd/MCM-41 samples plotted as a function of total time.

Pd/MCM-41 was not able to substantially reduce initial concentrations of hexamethylphosphoramide (HMPA) in a batch experiment. Results of the experiment are presented in Figure 9. A small reduction in the initial HMPA concentration was attributed to adsorption onto the Pd/MCM-41 surfaces rather than degradation of the compound.

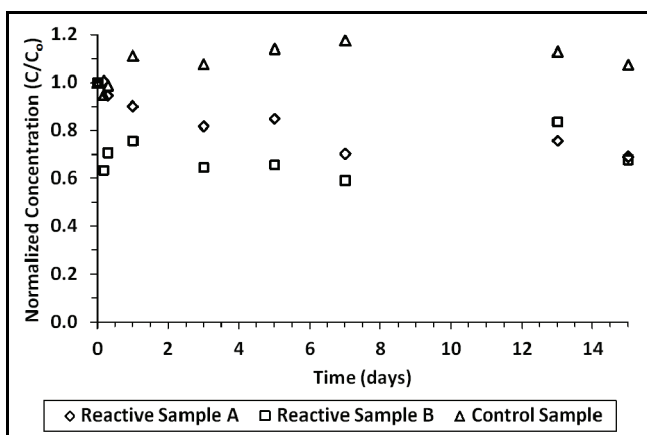


Figure 9: Normalized HMPA concentration versus time results for degradation batch experiments using 1.01% Pd/MCM-41 and non-reactive control samples.

6 ACKNOWLEDGEMENTS

Funding for this project was provided by NSERC (Natural Sciences and Engineering Research Council of Canada), ETECH (Ontario Centre of Excellence), and Envirometal Technologies Inc.

REFERENCES

- [1] Cheng, C. F.; Park, D. H.; Klinowski, J. *Journal of the Chemical Society - Faraday Transactions* **1997**, *93*, 193-197.
- [2] Mansour, F.; Dimeo, R. M.; Peemoeller, H. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* **2002**, *66*, 041307/1-041307/7.
- [3] Guthrie, C. P.; Reardon, E. J. *Journal of Physical Chemistry A* **2008**, *112*, 3386-3390.
- [4] Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. -; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *Journal of the American Chemical Society* **1992**, *114*, 10834-10843.
- [5] Mastalir, A.; Rác, B.; Király, Z.; Molnár, A. *Journal of Molecular Catalysis A: Chemical* **2007**, *264*, 170-178.
- [6] Koh, C. A.; Nooney, R.; Tahir, S. *Catalysis Letters* **1997**, *47*, 199-203.
- [7] Haber, J.; Block, J.H.; Delmon, B. *Manual of Methods and Procedures for Catalyst Characterization*. IUPAC. Pure and Applied Chemistry **1995**, *67* (8/9), 1257-1306.