15 Free Radical Attack on C_{60} Embedded in Nanochannels of Mesoporous Silica

C. H. Lee[a], H. P. Lin[b], T. S. Lin[c] and C. Y. Mou[a]*

[a]Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, China

[b]Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115, China

[c]Department of Chemistry, Washington University, MO 63130 USA

1. INTRODUCTION

MCM-41 materials belong to a family of mesoporous aluminosilicates (M41S), which was disclosed by Mobil researchers (Kresge *et al.*, 1992). The materials consist of hexagonal arrays of uniform 2 to 10 nanometer-sized cylindrical pores. The channel pores are created by using the self-assembly of silicates with surfactant as the templates and followed by calcinations of organic part. The wall surface of MCM-41 mesoporous materials can be modified with proper functional groups, such as amine (-NH_2), thiol (-SH) and linear alkyl chains ($CH_3(CH_2)_n$-) (Feng *et al.*, 1997). These functional groups allow one to probe the structure, dynamics and chemical reactivity of confined molecules in the nanochannels of these mesoporous materials.

Chemical reactions carried out in confined space are of current interest (Rouhi, 2001). Reactions in which molecules are physically constrained could lead to many new fundamental understandings about the use of local environment in controlling chemical reactions. Among these, radical reactions are most interesting because of the possibility of reducing the random combination of radical species.

Fullerene is known to be a good electron scavenger and its reactivity towards free radicals, such as hydroxyl, is important both in fundamental chemistry and in

---

* Corresponding author. Tel: 886-2-3366-5251; Email: cymou@ms.cc.ntu.edu.tw

medical applications (Reed *et al.*, 2000). It would be very interesting to explore the radical reactions of C_{60} in confined space such as MCM-41. Because of the high void volume fraction of MCM-41, it will be shown that C_{60} can be embedded within the pores to high loading, especially in the amine modified MCM-41 solids. Here we report the reactions of C_{60} with hydroxyl free radicals in nanochannels of the matrix of amine modified MCM-41 materials.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Amine modified MCM-41

The MCM41-NH_2 with amine functional group was synthesized in the following steps: 0.5 g of the calcined MCM-41 was placed in 100 ml toluene and stirred for 30 minutes 2.5 g of 3-aminopropyltrimethoxysilane was added to the resulting mixture. The above reaction was allowed to reflux overnight.

2.2. Binding of C_{60} on the Amine-modified MCM-41

Since fulleride ion dissolves better and has higher affinity to amine-functionalized channel pores, we use the reduced form (C_{60}^-) to increase the loading of C_{60} in MCM41-NH_2. Thus, we expect the fulleride ion would bind more easily to amines. We prepared the more hydrophilic anion C_{60}^- species as follows: mixing 40 mg C_{60} with 130 mg THAB (tetrahexylammonium bromide) in 40 ml THF (tetahydrofuran) and 2 - 3 drops Hg. The solution was heated to and maintained at 80 °C for 3 hours under nitrogen atmosphere (Boulas *et al.*, 1993). Next we prepared the target material by mixing the above solution with 200 mg of MCM41-NH_2. After stirring the mixture for 12 hours under nitrogen atmosphere, the solids were washed twice with toluene and acetone.

### 2.3. Generation and Detection of Hydroxyl Radicals ($^\bullet$OH)

Hydroxyl radicals were generated via the Fenton reaction ($Fe^{2+} + H_2O_2$). Since $^\bullet$OH radicals are short-lived species, we employed a spin-trapping agent DMPO (5,5-dimethyl-1- pyroline N-oxide) to trap and convert the reactive radicals to stable nitroxides, $^\bullet$DMPO-OH. The concentrations of the samples used in the experiments

were as follows: DMPO = 100 mM; H_2O_2 = 5 mM; $FeSO_4$ = 1 mM. The composition of a typical mixture of reagents used in the "control experiment" was: 30 µl DMPO; 400 µl $FeSO_4$; 100 µl H_2O_2. The mixture was vigorous shaken for 15 seconds, and the EPR spectra of the liquid were taken 4 minutes after the mixing.

3. RESULTS AND DISCUSSION

3.1. Characterization of MCM41-NH_2^+-C_{60}H Mesoporous Material

The reaction of MCM-41 with 3-aminopropyltrimethoxysilane (APTS) and the binding of C_{60} on MCM41-NH_2 are shown in Fig. 1.
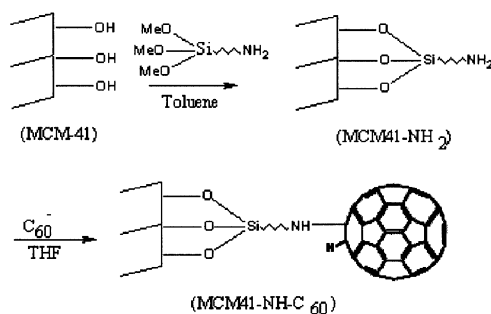
Figure 1. The schematic diagram of the preparation of MCM41-NH_2 and MCM41-NH-C_{60}H solid.

The surface areas and pore diameters of MCM41-NH_2 and MCM41-NH-C_{60}H in comparison with unmodified MCM-41 matrix are shown in Table 1. We note that the surface area has been reduced from 1015 m^2/g in the unmodified MCM-41 to 753 m^2/g in the modified MCM41-NH_2, a 30% reduction. The pore diameter of the mesoporous material has also been reduced from 2.7 to 1.7 nm after the -$O_3Si(CH_2)_3NH_2$ modification.

The data of elemental analysis in Table 1 list four different samples. For unmodified MCM-41, we find no carbon and nitrogen residue to confirm the calcinations completely removes surfactants. From the nitrogen content of MCM41-NH_2 sample, we find that there is 1.48 mmole of -NH_2 per gram MCM41-NH_2.

From the difference of carbon contents between MCM41-NH$_2$ and MCM41-NH-C$_{60}$H samples, we can calculate the amount of C$_{60}$ loaded. There are two kinds of samples for MCM41-NH-C$_{60}$H: from C$_{60}$ or C$_{60}^-$. We find that the loading from fulleride anion is much higher, e.g. 0.08 mmole C$_{60}$ per gram MCM41-NH-C$_{60}$H. This is due to the much higher solubility and affinity to the amine-modified surface of C$_{60}^-$. We find the effective modification of MCM-41 is 1.18 (number of -NH2/nm^2), and that of C$_{60}$ binding on MCM41-NH$_2$ is 0.048 (number of C$_{60}$/nm^2).

Table 1. Surface area, pore diameter and composition of MCM-41 solids

| Sample	Surface area /m^2/g	Pore diameter /nm	Elemental Analysis		
			C/%	H/%	N/%
MCM-41	1015	2.7	0	1.13	0.02
MCM41-NH$_2$	753	1.7	7.37	2.62	2.09
MCM41-NH-C$_{60}$H^a	636	1.7	8.66	2.65	2.05
MCM41-NH$_2$-C$_{60}$H^b	234	1.3-2.0	13.13	2.96	2.18

a. Refluxing C$_{60}$ with MCM41-NH$_2$ in toluene.

b. Refluxing C$_{60}^-$ with MCM41-NH$_2$ in THF under nitrogen atmosphere.

3.2. Free Radical Attack on Confined C$_{60}$: Electron Paramagnetic Resonance Studies

The efficacy of free radical scavenging by confined C$_{60}$ will be examined with respect to the localization of free radical production centers (Fe^{2+} sites in a Fenton reaction), on the inner surface of nanochannels nearby C$_{60}$ or on the outer surface of the channels in the bulk solution.

The formation of $^\bullet$OH radical and its subsequent fate in the presence of DMPO MCM41-NH-C$_{60}$H are given in the following chemical reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {^\bullet}OH \qquad (1)$$
$$DMPO + {^\bullet}OH \rightarrow {^\bullet}DMPO{-}OH \qquad (2)$$
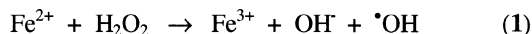
The EPR spectrum of the liquid phase, $^\bullet$DMPO-OH spin adducts, displays a characteristic 1:2:2:1 hyperfine splitting pattern ($a_N = a_{H\beta} = 14.96$ G, Fig. 2A, spectrum I).

The EPR spectra of $^\bullet$DMPO-OH in the presence of MCM41-NH-C60H are shown in Fig. 2A, spectra II and III. The spectrum II of Fig. 2A, is referred to the case where Fe^{2+} was added in the last step of the generation of $^\bullet$OH free radicals. The spectrum III of Fig. 2A shows the case where Fe^{2+} was added to MCM41-NH-C$_{60}$H solids at the very beginning to "anchor" Fe^{2+} on the surface, then DMPO and water, and H_2O_2 was added at the last step in the generation of $^\bullet$OH radicals.
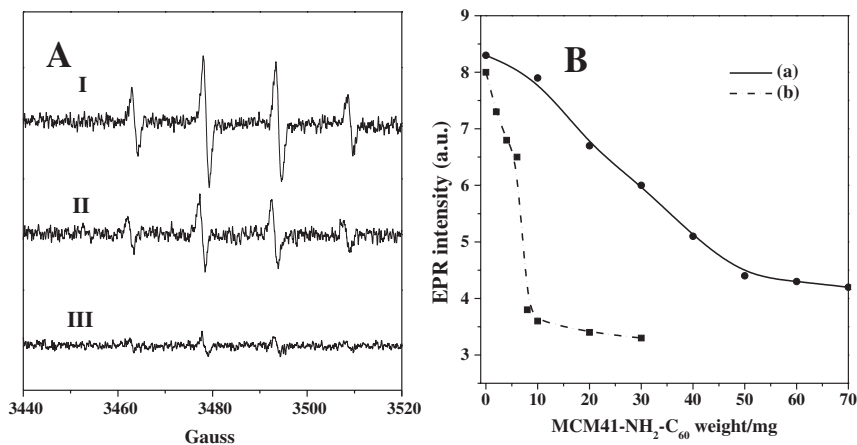
Figure 2. (A) EPR spectra of $^\bullet$OH radicals generated from Fenton reaction in the presence of DMPO: (I) no MCM41-NH-C$_{60}$H was added (II) Fe^{2+} was added to the 10 mg MCM41- NH-C$_{60}$H solids in the last step of the Fenton reaction, and (III) Fe^{2+} was added to the 10 mg MCM41-NH-C$_{60}$H solids at the beginning to form catalytic sites for the decomposition of H_2O_2. (B) EPR intensity (height of 2nd peak of $^\bullet$DMPO-OH radical, see Fig. 2A) *vs.* the amount of MCM41- NH-C$_{60}$H added to the Fenton reaction: (a) Fe^{2+} was added to the MCM41- NH-C$_{60}$H solids in the last step of the reaction, and (b) Fe^{2+} was added at the beginning.

The EPR intensity (based on the signal height of the second peak) as a function of the amount MCM41-NH-C$_{60}$H is shown in Fig. 2B. We observed the EPR intensity decreased to nearly zero at 50 mg when Fe^{2+} was added to MCM41-NH-C$_{60}$H solids in the very last step of the reaction (Fig. 2B, line a), while it requires only 10 mg of MCM41-NH-C$_{60}$H to produce the same effect when Fe^{2+} was added to MCM41-NH-C$_{60}$H first (Fig. 2B, line b), i.e., the presence of Fe^{2+}

binding with -NH$_2$ on the MCM-41 wall surface facilitate the free radical scavenging by nearby C$_{60}$ by a factor of five.

The large surface area of these mesoporous materials and the specificity of rigid binding with C$_{60}$ and other catalytic site for the oxidation of H$_2$O$_2$, such as Fe^{2+}, further allow one to examine the diffusion controlling factor on the free radicals scavenging. These mesoporous silica with 2 to 10 nm pores provide us an opportunity to examine the chemical reactivity of C$_{60}$ in the confined space of nanochannnels.

4. CONCLUSION

The applications of MCM41-NH$_2$ mesoporous materials provide us with an opportunity to examine the chemical reactivity of C$_{60}$ in the confined space of nanochannels structure under different experimental conditions. Our results show that when C$_{60}$ is anchored in the nanochannels with Fe^{2+}, $^{\bullet}$OH radicals can be eliminated much more effectively than when Fe^{2+} is situated outside of the nanochannels. Thus, we have demonstrated by using surface functionalization on mesoporous silica, one can keep the scavenger and radical generation in proximity to increase the efficacy. This would allow us to control the reaction pathways if there exist complex chemical systems.

REFERENCES

Boulas, P., Subramanian, R., Kutner, W., Jones, M. T. and Kadish, K. M., 1993, Facile preparation of the c-60 monoanion in aprotic-solvents, *J. Electrochem. Soc.*, **140**, pp. 130.

Feng, X., Fryxell, G. E., Wang, L. Q., Kim, A. Y. and Liu, J., 1997, Functionalized monolayer on Ordered Mesoporous Supports, *Science*, **276**, pp. 923-926.

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. and Beck, J. S., 1992, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, *Nature*, **359**, pp. 710-713.

Reed, C. A. and Bolskar, R. D., 2000, Discrete fulleride anions and fullerenium cations, *Chem. Rev.*, **100**, pp. 1075.

Rouhi, A. M., 2000, From membranes to nanotubules, *Chem & Eng. News*, **78**, pp. 40.