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Communications

Adsorption of C$_{60}$ in Zeolite NaY

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Since the discovery on the preparation of macroscopic quantities of C$_{60}$ by Kräschmer *et al.*,[1] the physical and chemical properties of C$_{60}$ have been of great interest to many scientists. The study of C$_{60}$ molecules received further impetus with the subsequent announcement of superconductivity[2] in C$_{60}$ doped with alkali metals. Zeolites are crystalline aluminosilicate materials which have high internal surface area and molecular size çage dimensions.[3] These materials play important roles as adsorbents or shape-selective catalysis in a wide variety of separation, chemical, and petrochemical processes.[4] Recently, zeolites have been exploited to serve hosts for interesting guests because of their well-ordered arrays of nanosized void spaces.[5] The physicochemical properties of guest materials within zeolites are significantly distinct from their bulk characteristics because of quantum confinement effects. Hence, it would be interesting to investigate the physicochemical properties of C$_{60}$ adsorbed inside the crystalline voids of zeolites and compare the results to those obtained from the bulk C$_{60}$. In this communication, we present the preliminary results obtained from the C$_{60}$ molecules adsorbed in the supercages of zeolite NaY which was chosen because the its supercage aperature 7.4 Å is comparable to the diameter of C$_{60}$, 7.1 Å.

C$_{60}$ was prepared based on the procedure of Haufler *et al.*[6,7] The C$_{60}$ was dried at 473 K overnight to remove residual solvent. NaY (SiO$_2$/Al$_2$O$_3$=4.86) was purchased from Strem. The NaY was refluxed twice in 1 M NaNO$_3$ solutions overnight in order to ensure that the sample was in its complete Na form, and dehydrated fully at 773 K under high vacuum overnight. The nitrogen BET surface area of the NaY sample is 641 m$^2 \cdot$g^{-1}.

The adsorption of C$_{60}$ into the supercages of NaY was carried out by a vapor phase impregnation method.[8,9] 200 mg of the dehydrated NaY was physically mixed with 27 mg of C$_{60}$ inside a 10 m*l* tube under an inert atmosphere at room temperature (0.3 C$_{60}$ molecule per NaY supercage). The reaction mixture in the sample tube was transferred to a vacuum apparatus through a high-vacuum stopstock and evacuated at 77 K to vacuum better than 10^{-5} torr. After sealing the tube, the sample was slowly heated to 683 K, held at this temperature for 6 h and then slowly cooled to room temperature. The heating and cooling rates were 2 K$\cdot$min^{-1}.

The X-ray diffraction pattern of C$_{60}$-containing NaY prepared by the vapor phase impregnation method shows that the structure of NaY remains unaltered through the adsorption process and no reflections other than those from the zeolite are observed. The color of the C$_{60}$ containing NaY sample was grey unlike pure C$_{60}$'s.
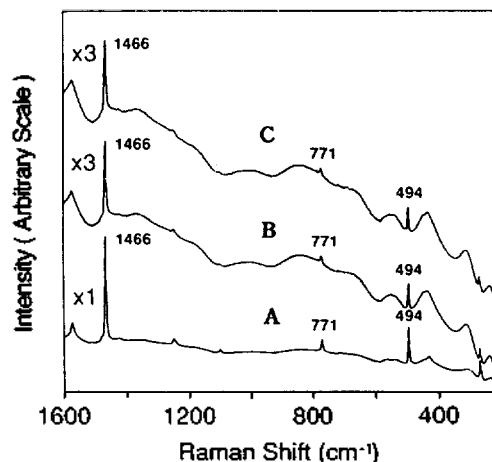

Figure 1. The Raman spectra of (A) the physical mixture of C$_{60}$ and NaY (1 : 6) and (B) the NaY samples containing C$_{60}$ before the extraction and (C) the one after the extraction. The excitation source was the 1064 nm line of an Nd : YAG laser at an intensity of about 0.3 W at the sample.

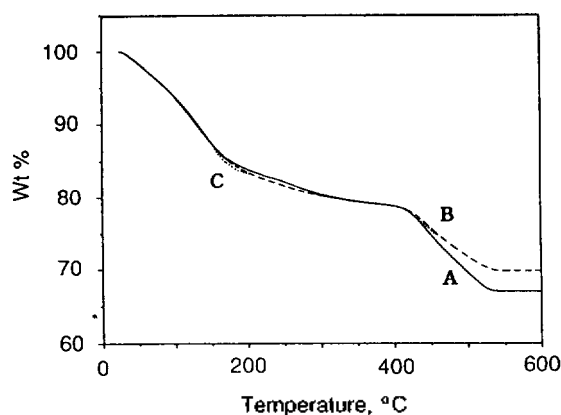*To whom correspondence should be addressed.

Figure 2. The thermograms for (A) the physical mixture of C_{60} and NaY (1 : 6) [solid line] and for the NaY samples containing C_{60} (B) before [dashed line] and (C) after [short dashed line] soxhlet extraction with boiling benzene over night. Experiments were run in air using approximately 10 mg of samples at a heating rate of 5 K·min⁻¹. The curves (B) and (C) are overlapped except two regions in which the curve (C) can be seen.

Figure 1 shows the Raman spectra of the physical mixture of C_{60} and NaY (1 : 6) and the NaY samples containing C_{60} before and after the removal of C_{60} at the surface of zeolite by solvent extraction.[10] Our Raman spectrum for C_{60} is consistent with the previously reported results.[11-13] The Raman spectra obtained from C_{60}-containing zeolite samples show almost the same band positions and relative intensities as those from the neat, crystalline C_{60}. This indicates that C_{60} molecules remain intact after heat treatments to 683 K.

Figure 2 illustrates the thermogravimetric analysis (TGA) results for the mixture of C_{60} and NaY (1 : 6) and for the C_{60} containing NaY samples. The thermograms show two distinct steps of weight loss: 25-300℃ and 400-550℃. The first loss is caused by the removal of physically adsorbed water since the sample was fully rehydrated prior to the TGA experiments. The second step is due to C_{60} loss. The previous TGA studies[14-16] have shown that pure C_{60} gives 100% weight loss in the temperature region of 400-550℃ when the experiment is taken in air at a heating rate of 5 K·min⁻¹. There are no noticeable differences in the thermograms for the mixture of C_{60} and NaY (1 : 6) and the C_{60}-containing NaY samples. It was expected that zeolite supercages restrict C_{60} to sublime at higher temperature than C_{60} in the mixture with zeolite if there exists the interaction between C_{60} and zeolite walls. However, the TGA data show that the sublimation of C_{60} was not affected by the presence of the zeolite.

In order to locate C_{60} molecules clearly, we washed the C_{60}-containing NaY sample by solvent extraction method using boiling benzene which is a good solvent for C_{60} overnight. If the C_{60} molecules mainly exists on the outer surface of the NaY crystals, they could be removed during the extraction process and the second weight loss would not be observed. The weight loss associated with C_{60} still appears in the thermogram of C_{60}-containing NaY sample aftr the extraction and the amount of loss is almost the same as that observed in the thermogram of the sample before the extraction (Figure 2(C)). And we could not find the trace of C_{60} in the extract when checked with the UV-Vis spectro-

photometry. Then, it is obvious that most C_{60} molecules added in the adsorption step are located in the supercage rather than on the exterior surface of the NaY crystals and that the interaction between C_{60} in zeolite with zeolite substrate is very weak. The latter fact is supported by the low temperature Differential Scanning Calorimetry (DSC) results.[17]

Finally, Keizer et al.,[18] recently prepared the C_{60} trapped in zeolite NaX. However, they used very small amounts of C_{60} in the adsorption step (ca. 10⁻⁴ molecule per supercage) and did not show any conclusive evidence for the presence of C_{60} in the zeolite. It is necessary to prepare the NaY sample that contains C_{60} exclusively on their inner surfaces with high concentrations, in order to increase the sensitivity of the available analytical methods. Now study on rotational dynamics of C_{60} molecules in NaY is in progress by variable temperature measurements of NMR, DSC, Raman, and Photoacoustic spectroscopy.

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# A Mechanistic Study for the Addition Reaction of Secondary Amines to Methyl Propiolate

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Nucleophilic addition to triple bonds has been extensively studied for a variety of synthetic interests.[1-3] Particularly, additions of amines to acetylenes with a strong electron withdrawing substituent have intrigued synthetic chemists due to the high versatility of the addition products, enamines.[4,5] However, mechanistic studies for reactions of electron deficient acetylenes with amines have not been systematically investigated, although scattered informations on kinetic studies are available.[6,7]

For a systematic study, we have investigated the reaction of methyl propiolate (1) with 7 different secondary amines whose pK_a range is over 5.5 in the pK_a unit. A preliminary study has revealed that the enamines obtained in the present reactions are exclusively the trans isomers. In addition, the reaction of 1 with ammonia or hydroxide ion was found to proceed in a different manner, i.e., a substitution reaction occurred at the carbonyl carbon to give an amide or a carboxylate and methanol instead of an addition product as shown below.

(reaction scheme)
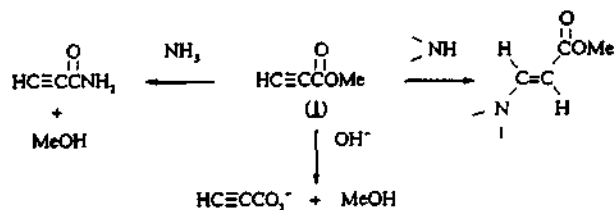
The observed rate constants (k_{obs}) were measured spectrophotometrically by monitoring the appearance of the product at a fixed wavelength corresponding to the maximum absorption of respective enamines. All the reactions were carried

Table 1. Summary of the Second-Order Rate Constants (k_2) for the Addition Reaction of Secondary Amines to Methyl Propiolate in H_2O at 25.0°C

Amine	pK_a^a	λ_{max} of enamine, nm	k_2, $M^{-1}s^{-1}$
1. piperazine	5.68[c]	277	0.040
2. morpholine	8.36	283	0.233(0.308)[b]
3. piperazine	9.82[d]	285	0.505
4. diethylamine	10.98	284	0.568
5. 3-Me piperidine	11.07	287	1.41
6. piperidine	11.22	289	1.24
7. pyrrolidine	11.27	291	6.94

$^a pK_a$ of conjugate acid of the amine; pK_a data taken from reference 13. pH of the reaction medium is kept near the pK_a of respective amines by keeping the buffer ratio with unit, i.e. [amine H^+]/[amine] = 1. [b] The rate constant for the reaction run in D_2O. [c] $pK_{a(1)}$, [d] $pK_{a(2)}$.
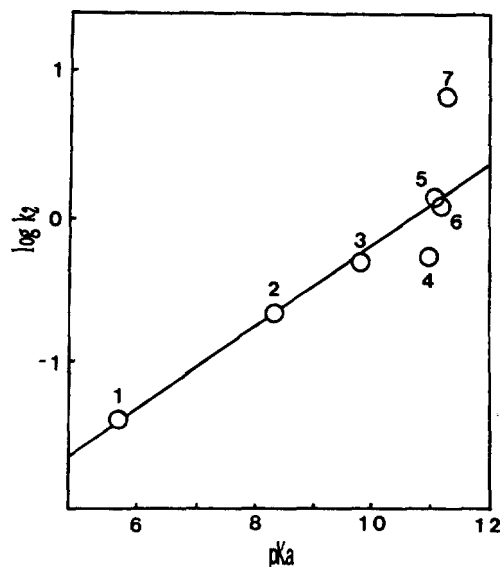

Figure 1. A Brφnsted plot for the addition reaction of secondary amines to methyl propiolate in H_2O at 25°C. The numbers refer to the amines of Table 1.

out under pseudo-first-order conditions in which the concentration of amines was in large excess of 1. Second order constants (k_2) were obtained from the slopes of the linear plots of k_{obs} vs. amine concentrations.

The kinetic results for the reaction of 1 with seven secondary amines are summarized in Table 1 and demonstrated graphically in Figure 1. As shown in Figure 1, six-membered cyclic amines show a good Brönsted correlation while the other two (an acyclic and a five-membered cyclic amines) exhibit significant deviations from the linearity.

It has been generally believed that a linearity obtained from a Brönsted plot is suggestive of a common reaction mechanism for a series of reactants.[8] Similary, a break in Brönsted plot has been considered as an indication of a change in reaction mechanism.[8] However, this would be valid only when the reactants in the system are structurally similar.[9] Since pyrrolidine and diethylamine are structurally different from the other amines, it is not necessary to invoke