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Research Paper

Investigation of molecular motion of Cl-adamantane in the nanoprous zeolite by ^{13}C NMR dipolar dephasing and variable contact time measurements

A. Samadi Maybodi *

Analytical Division Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

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ABSTRACT: Dipolar-dephasing method provides some information about the strength of dipolar coupling in solids. Dipolar dephasing technique measures the time for a polarized carbon nucleus to lose its magnetization once the proton locking field is terminated. The dynamics of guest molecules adsorbed within the cavities and channels of nanoprous zeolite strongly depend on the structure and chemical composition of the nonporous zeolite. In this work solid-state ^{13}C NMR spectroscopy and dipolar dephasing technique were used to determine the extent of motion 1-chlroadamantane loaded in nanoprous zeolite-Y. Loading of 1-chlroadamantane into the supercages of the zeolite-Y (with R=100 and R=2.35, R=Si/Al) was carried out by a vapor phase impregnation and solution impregnation methods. The accuracy of dipolar dephasing method was first investigated with the aid of pure 1-chlroadamantane to determine the degree of motion in the nanoprous of zeolite-Y. Results indicated that the C_δ signal of the 1-chlroadamantane in the nonporous zeolite-Y decays faster than that the C and C, demonstrating that dipolar interaction for this carbon (C_δ) is stronger. However, the rate of signal decay C_δ for the 1-chlroadamantane loaded in zeolite -Y (R=2.35) is less than that loaded in zeolite-Y (R=100).

Keywords: *CPMAS NMR; Dipolar dephasing; Impregnation; Molecular motion; Nanoprous; Zeolite-Y; 1-Chlroadamantane.*

INTRODUCTION

Measurement of internuclear distances is one of the most important factors in the structural studies of solids. One way to access internuclear distances is to measure the dipolar coupling between two nuclei using solid-state nuclear magnetic resonance (NMR) techniques. In polycrystalline and disordered solids, various NMR methods have been developed to measure homonuclear and heteronuclear dipolar couplings [1].

NMR can be applied for studying molecular motion and dynamic behavior of the molecules in nanoprous materials [2]. A large number of NMR parameters, including the strength of heteronuclear dipolar interactions, are sensitive to molecular motions [3]. High-resolution ^{13}C NMR in molecular solids often provides some insight into the motions, which is not always available from, for example, wide-line proton spectra. The dipolar dephasing technique has been widely used to obtain chemical structural information and assign the resonance signals of polymers, fossil fuel, and wood samples, as well as other complex materials [4]. Although it is well-known that molecular motion has a great impact on the dephasing of carbon signals, especially for the methylene and methine carbons [5], this method has not been used for exploration of molecular motions. The intensity of dipolar interaction can also be deduced from the rise of ^{13}C magnetization in cross-polarization experiments and by ^{13}C-^{1}H dipolar dephasing NMR, a technique that is widely used for distinguishing carbon atoms in chemical structure determinations [6-9].

The dynamics of guest molecules adsorbed within the cavities and channels of nanoprous zeolite strongly depend on the structure and chemical composition of the zeolite, as well as on the molecular properties of the adsorbed species. A variety of host-guest

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*Corresponding Author: Abdolraouf Samadi Maybodi
Email: *samadi@umz.ac.ir*
Tel.: (+98) 1135302350
Fax: (+98) 1135302350

interactions are possible, such as strict hindrance or an attractive interaction between an extra framework cation in the nanoprous zeolite and the ®-electrons of an adsorbed aromatic molecule [10-13].

In this paper the dipolar dephasing technique was used to identify the motions of Cl-adamantane in nanoprous Zeolite-Y.

EXPERIMENTAL

Loading of 1-Chlroadamantane into Zeolite -Y.

Chlroadamantane was loaded into nanoprous zeolite with two following methods:

a) Vapor phase impregnation method. Loading of 1-chlroadamantane into the supercages of zeolite-Y was carried out by a vapor phase impregnation method. Prior loading of 1-chlroadamantane into zeolite-Y, the nanoprous zeolite was dehydrated at 550 °C for overnight. Inside a glass tube at room temperature zeolite-Y was physically mixed with a known amount of organic species. The amount of 1-chlroadamantane used in this study was 1.0 molecule per zeolite-Y supercage. After sealing the tube, the sample was slowly heated to final temperature of 50 C, and held at this temperature for 12 h, and then slowly cooled to room temperature. The others samples were prepared with the same method except the final temperature set to 100, 140, 150 and 200 °C.

b) Solution impregnation method. Loading of 1-Chlroadamantane in nanoprous zeoite-Y was also performed by dissolving 1-chlroadamantane in n-hexane. Zeolite-Y was added to the solution and stirred for 12 h. Finally, n-hexane was removed from the sample by high vacuum pump.

In this work two different kinds of nanoprous zeolites were used, i.e., zeolite-Y with R=100 and the other zeolite-Y with R=2.35 (R=Si/Al).

Instrumentation

All experiments were performed on a Varian Infinity Plus 400 WB NMR spectrometer operating at 100.45 MHz for ^{13}C. The pulse sequences used for the dipolar dephasing experiment is illustrated in Fig. 1. In this pulse sequence, after cross polarization, the proton decoupler is switched off for a variable time, $^{2}{}_{dd}$, during which the dipolar interactions between the carbons and protons induce the rapid dephasing of the carbon signal. A 90° refocusing pulse along the spin-locked coordinate was inserted halfway through the $^{2}{}_{dd}$ period to remove linear phase distortions and to refocus long-term isotropic and anisotropic chemical shift spin order.

The contact times for cross polarization were 5 ms for all dipolar dephasing experiments. The other spectroscopic conditions were as follow: ^{1}H 90° pulse = 6 μs, pulse delay = 10 s, spectrum width = 10.00 kHz, acquisition time = 204.8 ms and spin rate = 6 kHz. All spectra were recorded at ambient probe temperature of ca. 20 °C.

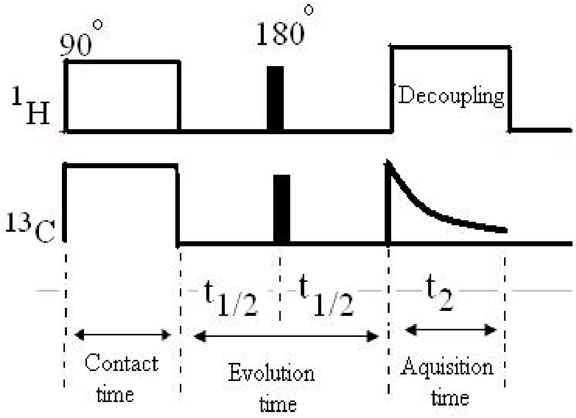

Fig. 1: The dipolar dephasing pulse sequence with one dephasing period.

RESULTS AND DISCUSSION

To find the situation of the prepared samples, ^{13}C CPMAS NMR spectra of all samples (i.e., prepared by two methods, vapor phase impregnation and solution impregnation) were recorded with the same spectroscopic conditions. NMR spectra obtained from the samples revealed that 1-chlroadamantane that loaded in nanoprous zeolite-Y (R=100) by vapor phase impregnation method was decomposed at the above temperature of 50 °C. On the other hand, ^{13}C CPMAS NMR spectra obtained from the sample using zeolite-Y with R=100 which prepared by solution impregnation method indicated that n-hexane is still left in the sample. The same experiments were also performed using nanoprous zeolite-Y with R = 2.35.

On the basis of results obtained from ^{13}C CPMAS NMR spectra, we selected (i) 1-chlroadamantane loaded in nanoprous zeolite-Y, R=100 using vapor impregnation method carried out at 50 °C and (ii) 1-chlroadamantane loaded in zeolite-Y, R=2.35 using solution impregnation method. ^{13}C CPMAS NMR spectrum of 1-chlroadamantane is presented in Fig. 2.

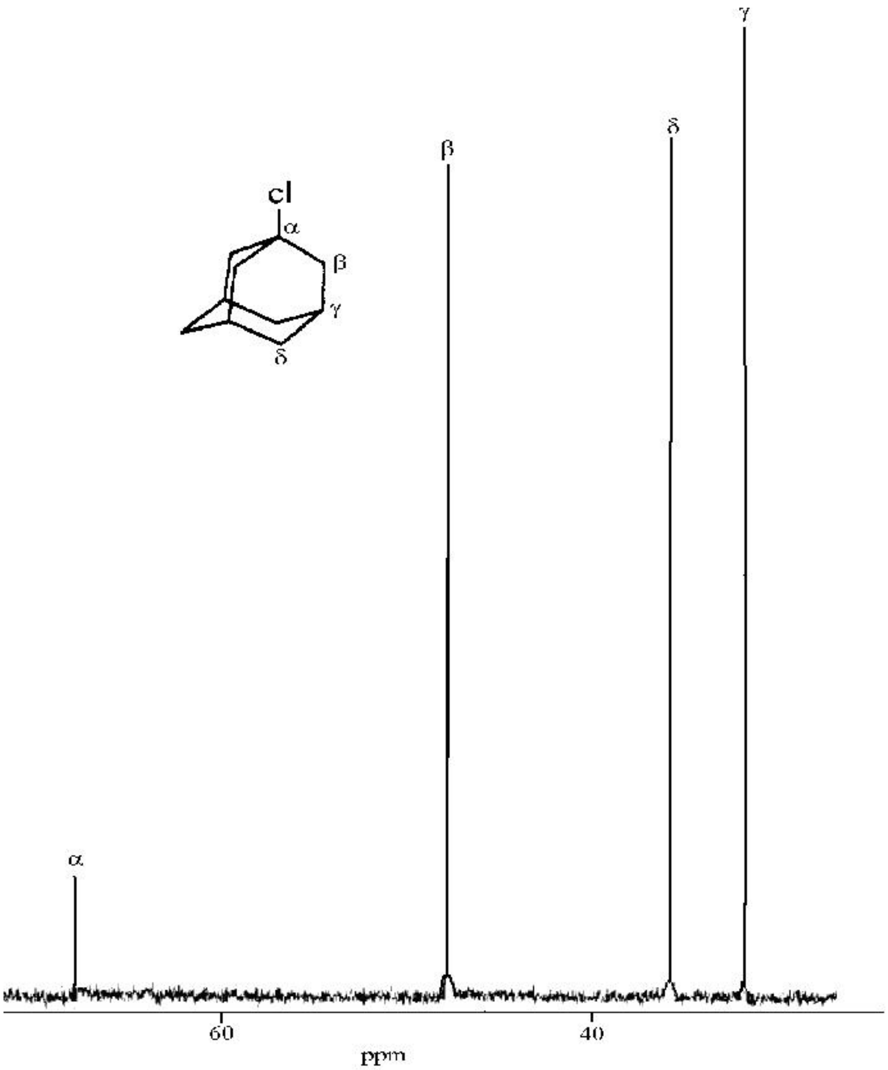

Fig. 2: ^{13}C CPMAS NMR spectrum of 1-chlroadamantane. spectroscopic conditions : contact times = 5 ms,. ^{1}H 90° pulse= 6 μs, pulse delay = 10 s, spectrum width = 10.00 kHz, acquisition time = 204.8 ms and spin rate = 6 kHz. Spectrum was recorded at ambient probe temperature of ca. 20 °C.

Dipolar dephasing experiment

The decay rate of the carbon signal intensity depends on the dipole-dipole interactions between proton and carbon. Generally, for the molecule in a rigid lattice, dephasing is most rapid for those carbons having directly bonded protons, such as CH and CH_2, due to the strong dipolar coupling. Nonprotonated carbons retain phase coherence for longer times because there is only a small effective dipolar interaction from neighboring groups. Methyl carbons usually experience a moderate degree of C-H dipolar coupling because the internal motion tends to weaken the dipolar interaction.

Data for carbons weakly coupled to protons follow a single exponential law before the first rotational echo:

$$I = I_0 e^{-t_1/T_2'}$$

where I_0 is the signal intensity at zero time and T_2' is the exponential decay constant for the signal intensity [5]. When the carbons are strongly coupled to protons, the signal decays frequently is modulated by the strong

^{13}C-^{1}H dipolar coupling, and the overall decay of the signal in the short time limit is better described by following equation:

$$I = I_0 e^{-t_1^2/(2T_2^2)}$$

The experimental results of dipolar dephasing for pure 1-chlroadamantane (i.e., not loaded in the zeolite), and loaded in nanoprous zeolite-Y with R=100 and R=2.35 are shown in Fig. 3(a-c) respectively.

Results obtained from the experiment of dipolar dephasing using pure 1-chlroadamantane indicate that β, δ and carbons decay slowly and methane (CH) and methylene (CH_2) groups have the same rate of signal decay. It can be deduced that in pure 1-chlroadamantane, the predominant motion is overall tumbling motion, and hence, all the CH and CH_2 carbons decay slowly. The intensity of the δ carbons for 1-chlroadamantane loaded in nanoprous zeolite-Y (R=100) decays much faster than those for pure 1-chlroadamantane, implying that the dipolar interaction for this carbon (C_δ) is stronger than the others.

If the motion is reorientation about C-Cl axis, then the intensities of all C_β, C_δ and C_γ carbons would decay much faster than they do in pure 1-chlroadamantane, because the freedom of motion is drastically reduced in comparison with the overall tumbling motion. Rotation about the C-Cl axis allows the axial ^{13}C-^{1}H bond (i.e. δ carbons) to remain parallel to the rotation axis, so that dipolar interaction is not diminished by the motion (axial rotation) and therefore will dominate the decay of the signal, as a result the signal of δ carbon decays rapidly much more than that of C_β and C_γ (Fig. 3b).

1-Chlroadamantane loaded in nanprous zeolite-Y with R=2.35, showed the same behavior, here also the C_δ signal decays faster than that the C_β and C_γ, indicating that dipolar interaction for this carbon (C_δ) is stronger. However, the rate of signal decay C_δ for the 1-chlroadamantane loaded in zeolite-Y (R=2.35) is less than that loaded in zeolite-Y (R=100).

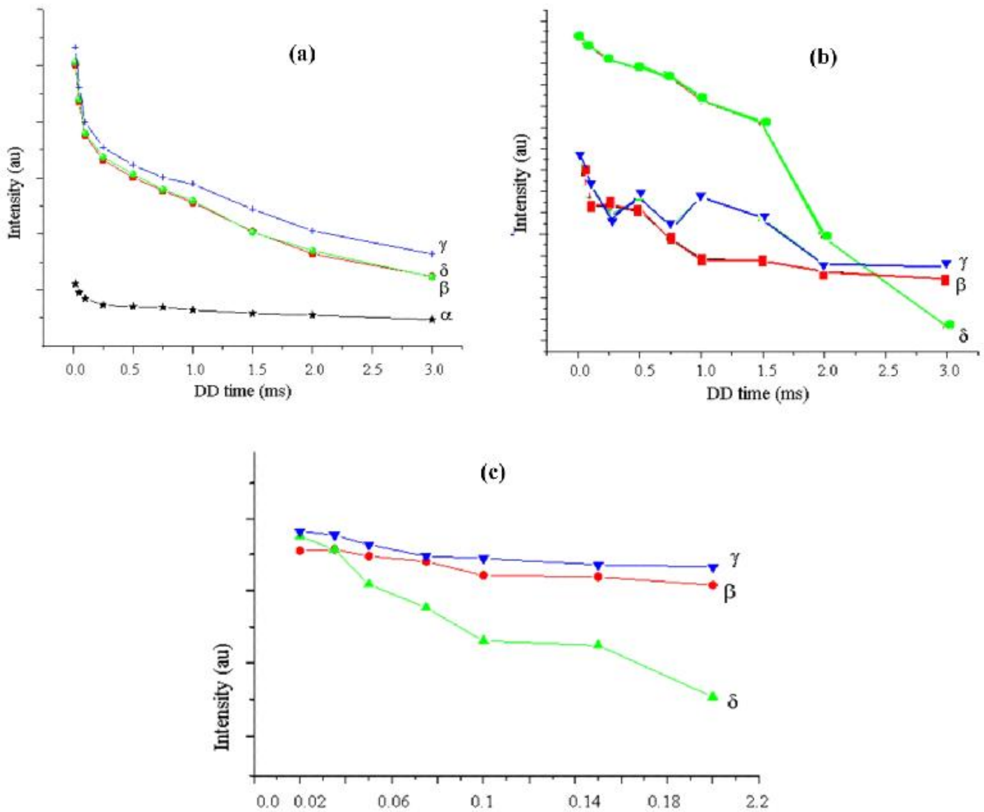

Fig. 3: Intensities (arbitrary units) of the dipolar dephased signal versus delay time for (a) pure 1-chlroadamantane at ca. 22 °C, (b) 1-chlroadamantane loaded in Zeolite-Y (R=100) at ca. 22 °C. (c) 1-chlroadamantane loaded in Zeolite-Y (R=2.35) at ca. 22 °C.

Variable contact time measurements

Results obtained from variable contact time (Fig. 4a-c) showed the same thermodynamic behavior, indicating the rate of cross polarization is deference for the carbons and confirm the results obtained from dipolar dephasing experiment. Results also are informative for understanding thermodynamic behavior of the 1-chlroadamantane in nanoprous zeolite.

CONCLUSION

Both conventional cross polarization and dipolar dephasing studies provide information on the magnitude of the ^{13}C-^{1}H dipole-dipole interactions. Results provided valuable insights into the extent of dynamic behavior of 1-chlroadamantene in nanoprous zeolite-Y. Results showed that the C_{δ} signal decays faster than that the C_{β} and C_{γ}, indicating that dipolar interaction for this carbon (C_{δ}) is stronger. The application of these techniques cannot be adequately characterized by other spectroscopic methods.

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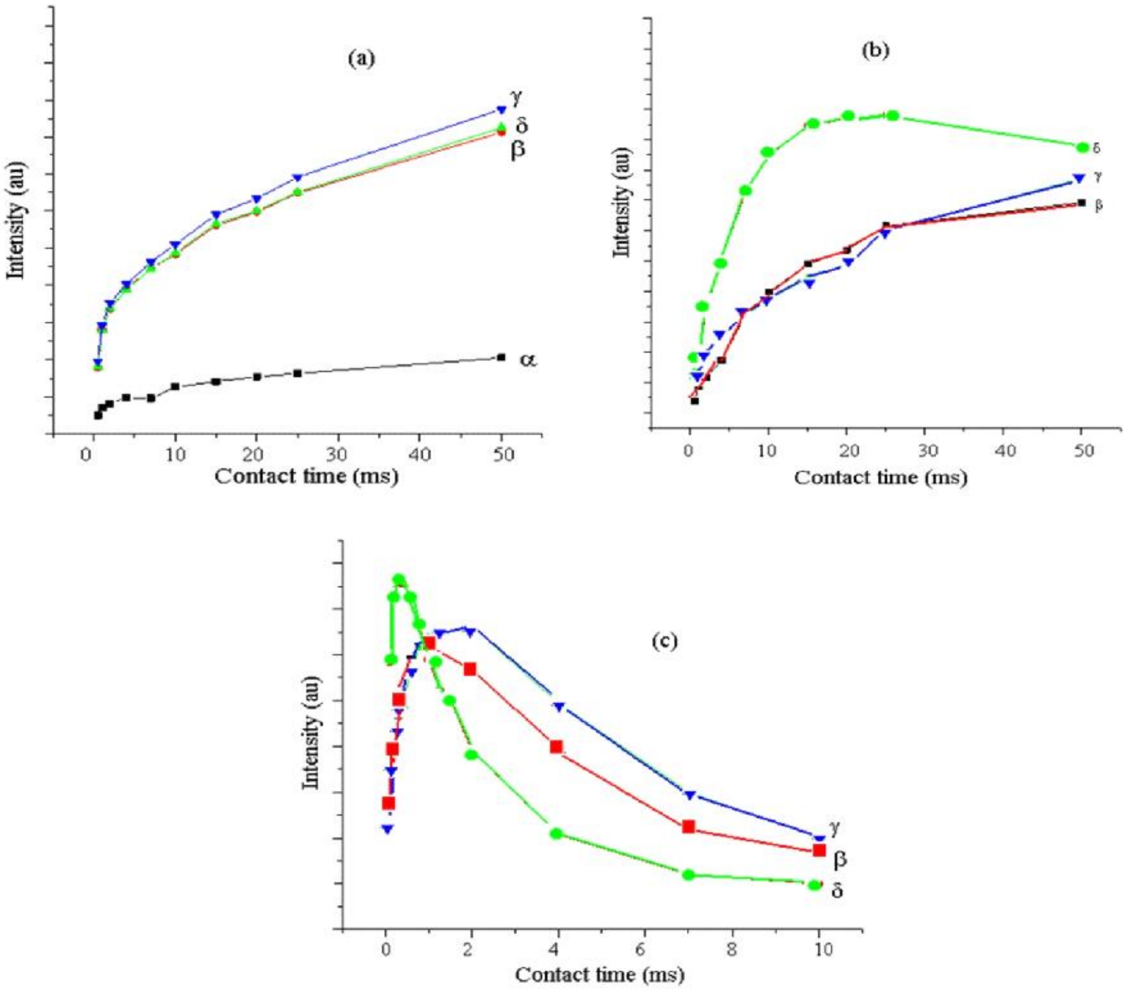

Fig. 4: Variation of ^{13}C signal intensity with contact time for (a) pure 1-chlroadamantane, (b) 1-chlroadamantane loaded in Zeolite-Y (R=100) and (c) 1-chlroadamantane loaded in Zeolite-Y (R=2.35) at ca. 22 °C.

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