A Solid-State ^{13}C NMR Study of the Molecular Motion of Ethylene Adsorbed on a Silver Surface

Jianxin Wang[†] **and Paul D. Ellis***

Contribution from the Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208. *Received July 3, 1992*

Abstract: The reorientation of ethylene on a silver catalyst surface has been studied by solid-state ^{13}C NMR. The static cross-polarization spectra at different temperatures have been measured. Different jump site models are proposed to simulate the experimental results. It was found that the models involving a low number of jump sites are more sensitive to the experimental details. By comparison of the simulated and experimental results, the 6- and 4-site jump models are chosen as the most satisfactory model to fit the experimental spectra. On the basis of this representation, the activation energy derived for the jump process is 4.3 kJ/mol. From the simulated results, it was concluded that the symmetry axis for the motion of the ethylene at low temperatures (−173 to ca. −45 °C) is perpendicular to the plane of the ethylene molecule. At higher temperatures motion about other axes is initiated such that at room temperature a nearly isotropically averaged ^{13}C sheilding tensor is observed.

Introduction

The selective oxidation of ethylene to ethylene oxide is important from both a fundamental and a practical point of view. Silver catalysts, supported by inert aluminas, e.g. α-alumina, are used in industry for this reaction. Adsorption of oxygen over a silver catalyst has been studied extensively.[1-4] This interest is due primarily to the question of which form of oxygen is on the silver catalyst. When compared with adsorption of oxygen, adsorption of ethylene over a silver catalyst has been studied to a lesser extent. However, studying the structure and molecular motion of ethylene on a silver catalyst is also important. This information can be used for understanding the reactivity and the mechanisms of ethylene oxidation and promotion. Several authors have found that ethylene does not adsorb on the silver catalyst surface unless oxygen preadsorbs on the silver catalyst surface.[5,6] Previously,[7,8] we have employed solid-state NMR to study ethylene on the silver catalyst, supported by γ-alumina; we found that ethylene did adsorb on the silver surface although it adsorbed very weakly and was moving relatively rapidly.

It is well-known that magnetic resonance line shapes are sensitive to the rates of the various dynamic processes which can modulate the anisotropic portions of the spin Hamiltonian. Generally the shielding tensor of a molecule is anisotropic, that is, it depends on the orientation of the molecule relative to the external, static magnetic field. If an adsorbed molecule undergoes fast random reorientation and tumbling, similar to that of liquids, only the isotropic average of the shielding tensor, i.e., the chemical shift, will be observed. However, if an adsorbed molecule reorients slowly, or if it reorients rapidly but undergoes restricted reorientation due to some characteristics of the surface, then the partial averaging of the shielding tensor will be expressed in the experimental line shape.[9] By comparing the calculated line shapes with the experimental spectra, models for the molecular motion and structure can be deduced.

Our interest in the catalytic properties of the Ag catalyst motivates us to investigate the motion and structure of ethylene adsorbed on its surface. The present work reports the experimental and the simulated results of the static ^{13}C solid-state NMR spectra of ethylene adsorbed on the silver catalyst surface, supported by γ-alumina. These spectra illustrate that the details of molecular motion on the catalyst surface change as a function of temperature.

Experimental Section

Silver nitrate (99.99%), potassium oxalate monohydrate (99%), ethanolamine (99%), and ethylenediamine (99%) were purchased from Aldrich Chemical Co. The γ-alumina pellets (No. SA 6173, 220 m^2/g) were provided by Norton Chemical Process Product Division. [1-^{13}C]-Ethylene (90%) was obtained from MSD Isotopes.

Catalyst samples used in this experiment were prepared by thermally decomposing silver amines on the γ-Al_2O_3 according to the Nielsen[10] method. Silver nitrate and potassium oxalate were dissolved in distilled water and mixed, and the resulting precipitate was washed 5 times to remove any remaining potassium salts. Then, 9 mL of ethylenediamine and 0.9 mL of ethanolamine were added to the silver oxalate to dissolve the precipitate. The solution was then poured over 5 g of γ-Al_2O_3 and kept overnight. The γ-Al_2O_3 was dried at 120 °C for 3 h and then put into a furnace at 290 °C for calcining. The final silver catalyst was gray in color. All the silver catalysts used in subsequent NMR experiments were 10% silver by weight.

NMR sample preparation was done on a home-built adsorption apparatus. The catalyst (0.6 g) was placed into a tube that was connected to a vacuum system. The sample was then heated to 270 °C for 4 h, cooled to room temperature, and pumped overnight until the final pressure above the sample in the tube was less than 5×10^{-6} Torr. A calibrated amount of mono-labeled ethylene was condensed on to the catalyst at liquid nitrogen temperatures. Before sealing the tube, samples were evacuated to remove physisorbed ethylene from the surface. After being evacuated, samples were sealed with a minitorch. Sealed samples were stored in liquid nitrogen to prevent further reaction with the surface. The NMR samples were loaded into rotors in a drybox under nitrogen atmosphere (Vacuum Atmospherics dual station glovebox). All ^{13}C solid-state NMR spectra were recorded on a Varian XL 300 spectrometer operating at 75.429 MHz for ^{13}C. High-power ^1H decoupling (ca. 46 kHz decoupling field) and cross-polarization (^1H field of 33 kHz) were employed for the experiments. All spectra were acquired with 1K data points and the spectral width was 100 kHz. The optimum contact time was found to be 200 μs. The optimum recycle delays found were different for different temperatures, typically 4 s for room temperature, 10 s for −57 °C, and 45 s for −173 °C. The spectra were referenced to tetramethylsilane by setting the most shielded resonance in adamantane as 29.5 ppm with respect to TMS.

Results and Discussion

α-Alumina is representative of the supports used in industry for the selective oxidation of ethylene to ethylene oxide. Here, we use γ-alumina as a support in our experiments. α-Alumina has a typical surface area of approximate 1 m^2/g, whereas γ-alumina has a much higher surface area of ~220 m^2/g. For the epoxidation reaction, γ-alumina would be unacceptable as a

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* Author to whom correspondence should be addressed.

[†] A Union Carbide Fellow.

(1) Jørgensen, K. A.; Hoffmann, R. *J. Phys. Chem.* **1990**, *94*, 3046.
(2) Dean, M.; Bowker, M. *J. Catal.* **1989**, *115*, 138.
(3) Van Santen, R. A.; Kuipers, H. P. C. E. *Adv. Catal.* **1987**, *35*, 265.
(4) Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1980**, *97*, 101.
(5) Kagawa, S.; Iwamoto, M.; Morl, H. *J. Phys. Chem.* **1981**, *85*, 434.
(6) Metcalf, P. L.; Harriott, P. *Ind. Eng. Chem. Process Des. Dev.* **1972**, *11*, 478.
(7) Chin, Y.; Ellis, P. D. *J. Am. Chem. Soc.*, submitted for publication.
(8) Wang, J.; Ellis, P. D. *J. Am. Chem. Soc.* **1991**, *113*, 9675.
(9) Mehring, M. *Principles of High Resolution NMR in Solids*, 2nd ed.; Springer-Verlag: New York, 1983.
(10) Nielsen, R. P.; LaRochelle, J. H. Shell Oil Co., U.S. Patent 3962136.

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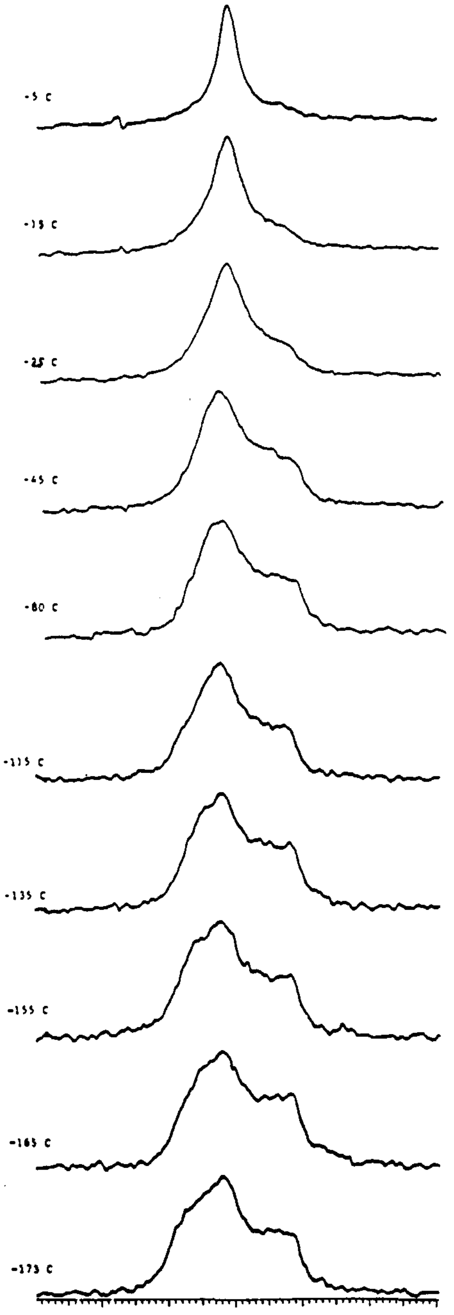

Figure 1. The temperature dependence of ^{13}C CP static NMR spectra of [1-^{13}C]ethylene adsorbed on a γ-alumina supported Ag catalyst is shown. The temperatures are indicated on the figure.

support, since it would cause severe isomerization and/or burning of the reaction product, ethylene oxide. These side reactions occur due to the presence of a greater number of Lewis and/or Bronsted acid sites on γ-alumina. In this investigation, our primary purpose is to investigate the molecular motion of ethylene on the surface of the silver catalyst and not the mechanistic details of the reaction. It is reasonable to assume that the details associated with the alumina support have no effect on the molecular motion of ethylene adsorbed to the silver particles. Although different supports may give rise to different activation energies, the overall motion of the ethylene adsorbed to the silver should be independent of the support. Due to the high surface area of γ-alumina, it is highly favorable to study the molecular motion of ethylene on this support. The low surface area of typical α-alumina supports precludes such measurements.

The solid-state ^{13}C spectra of ethylene adsorbed on the Ag catalyst surface at different temperatures are shown in Figure 1. The breadth of the resonance is about 185 ppm at a temperature of -173 ± 5 °C, and it decreases gradually with increasing temperature, until at room temperature it is only 20 ppm. The narrowing effect observed in these experiments must be caused by molecular motion. The complete chemical shielding interaction is described by a second-rank tensor σ, which can be represented by three components, σ_{11}, σ_{22}, and σ_{33}, in the principal axis system. The isotropically averaged chemical shift normally observed in solution and sometimes in solids is expressed in terms of the trace of the shielding tensor

$$\sigma_i = (1/3)(\sigma_{11} + \sigma_{22} + \sigma_{33})$$

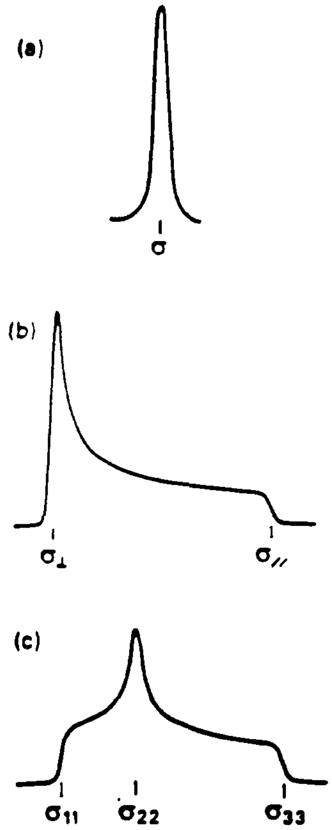

Figure 2. Typical shielding powder line shapes exhibited by sites with (a) cubic symmetry, (b) axial symmetry, and (c) lower symmetry.

Typical types of powder spectra are presented in Figure 2. Cubic nuclear site symmetry allows only one principal value for the shielding tensor as shown in Figure 2a. Axial site symmetry where the symmetry axis is 3-fold or higher allows two principal values ($\sigma_\perp$, perpendicular to the symmetry axis, and $\sigma_\parallel$, parallel to it), with a powder pattern as depicted in Figure 2b. For lower symmetry environments the three principal values of the shielding tensor manifest themselves in the powder pattern, as in Figure 2c. Those singularities are denoted as σ_{11}, σ_{22}, and σ_{33}. The usual convention used is $|\sigma_{33} - \sigma_i| \geq |\sigma_{11} - \sigma_i| \geq |\sigma_{22} - \sigma_i|$.[11] If molecular motion exists in the sample, the shielding tensor can be partially averaged. The resulting averaged tensor will have different values for σ_{ii} and potentially a different symmetry as well. For the spectra in Figure 1 at temperatures in the range of −80 to −45 °C, only two singularities are visible, and those can be characterized by $\sigma_\perp$ and $\sigma_\parallel$. Further, note that in Figure 1, as the temperature is increased from −173 to ca. −45 °C, that the most shielded element of the powder pattern appears to be independent of temperature. That is, that element of the shielding tensor is parallel to the axis of motion.

In all of the static and MAS experiments we have performed on this system, we have observed one resonance for the carbons of the ethylene bonded to the silver surface. From these obser-

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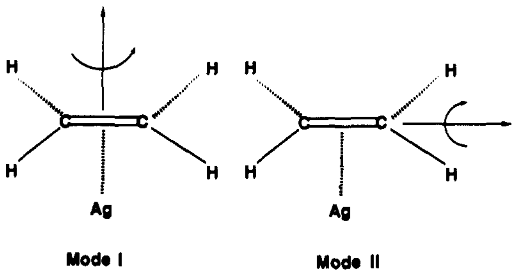
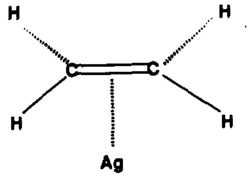
[11] Haeberlen, U. In *High Resolution NMR in Solids selective Averaging*; Academic Press: New York, 1979.

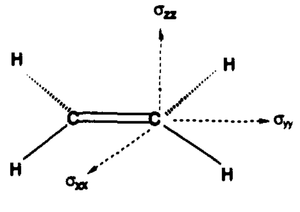
Chart I



vations, we conclude that the bonding is symmetric with respect to the carbon–carbon double bond, i.e. structure I. Structure I depicts the classic picture of an olefin donating π electrons to a metal substrate. Two modes of rotation for the olefin molecule are shown in Chart I. These are rotation about the axis perpendicular to the plane of the molecule or rotation about the C=C axis of the ethylene molecule. However, rotation pictured in mode II will lead to the breaking of the olefin metal bond and hence is less favored. Another argument favoring motion implied in mode I is the observed change of shielding line shape with the different temperature. The orientation of shielding tensor with respect to the molecule fixed frame for ethylene is known.[12] To determine the orientation of the shielding tensor with respect to the molecule fixed frame, Zilm and Grant[12] used the mutual interaction of the dipolar and shielding tensors. In the presence of the dipolar interaction, the resulting line shape is sensitive to the relative orientation of the dipolar and shielding tensors. This orientation of the shielding tensor is illustrated in structure II.



Structure I



Structure II

The shielding component σ_{22} lies along the double bond, that is σ_{yy}. The shielding component σ_{11} lies along the x direction, that is σ_{xx}. The shielding component σ_{33} is perpendicular to the plane of the molecule, that is σ_{zz}. We have performed analogous experiments with ethylene adsorbed to the silver surfaces described here and concluded that the orientation of the shielding tensor in ethylene and adsorbed ethylene is the same. The details of this work will be presented in a subsequent publication.[13] In Figure 1, when the temperature is increased and the motion of ethylene is increased, the σ_{22} and σ_{11} gradually merge into $\sigma_{\perp}$, and σ_{33} is independent of temperature. Since σ_{33} is perpendicular to the plane of the molecule, i.e., $\sigma_{\parallel}$, it implies that the motion must follow mode I presented in Chart I.

In order to understand the molecular motion in detail, we developed a computer program to simulate the solid-state spectra at different rates of molecular motion. The theory for the simulation program is given by Greenfield et al.[14] Before simulating the spectra, it is necessary to know the relative orientation of the jump frame to the shielding principal axis system and the number of jump sites. The relationship between the PAS frame of the chemical shift and the CC bond direction is known for ethylene, as mentioned above.[12]

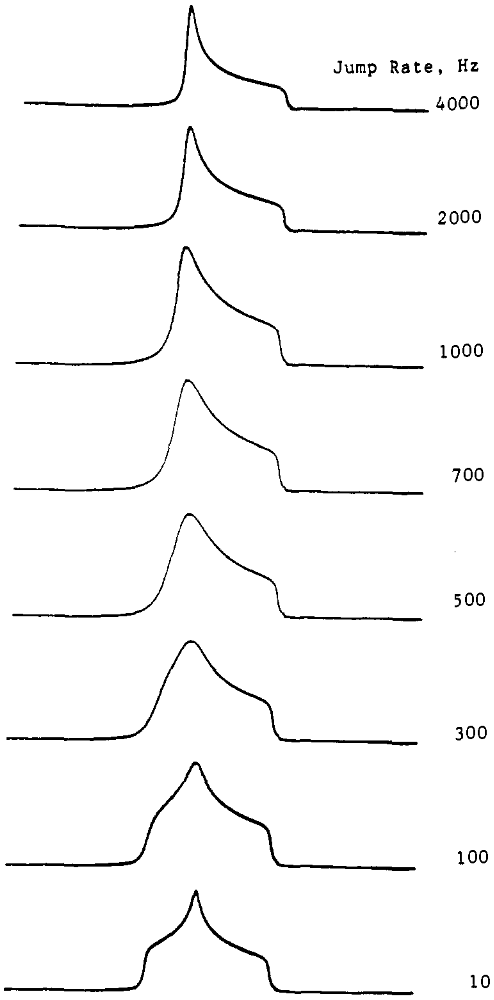


Figure 3. The simulation of 12-site 30° jumping at different exchange rates. The random model was used.

Choosing the jump sites depends on what kind of model is being used. Two types of models have been used for the simulation of the line shapes in the presence of molecular motion: (a) a random rotational diffusional model, in which molecules perform random finite jumps about a single axis with equal probability, and (b) a symmetry jump model, in which a molecule can undergo certain site jumps about a single axis that is determined by symmetry considerations. We approximate small angle random diffusion by making the number of sites large, i.e., N, and then performing jumps of $360/N$ at random. As $N \rightarrow \infty$, our model approaches the behavior of a system undergoing small step angle diffusion. The different jumping angles can give rise to the different line shapes.

For the random rotational diffusion model, the absorbed ethylene on a Ag surface can rotate freely; therefore, the jump angle can be any value at first. We use the hard collision limit; that is, the molecule can go to any jump angle with the same probability and sequential jumps have no relation to the previous jump. For practical reasons we have selected $N = 12$ and 36 in Figures 3 and 4, respectively. For all practical considerations the computed line shapes are the same. From Figures 3 and 4 one can see, at the slow motion limit, that the spectra have three principal values for the chemical shift tensor, and at the fast motion

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(12) Zilm, K. W.; Grant, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 2913.

(13) Wang, J.; Hughes, E.; Koons, J.; Ellis, P. D. To be submitted for publication.

(14) Greenfield, M. S.; Ronemus, A. D.; Vold, R. L.; Vold, R. R.; Ellis, P. D.; Raidy, T. E. *J. Magn. Reson.* **1987**, *72*, 89.

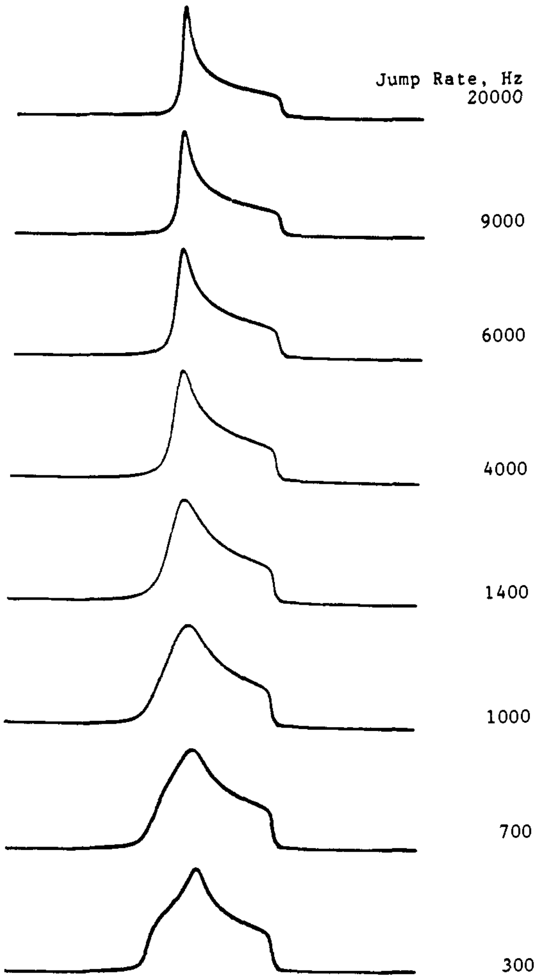

Figure 4. The simulation of 36-site 10° jumping at different exchange rates. The random model was used.

limit, the spectra display axial symmetry. Although the simulation spectra in Figures 3 and 4 fit the experimental result well at slow and fast motion limit, they fail to fit well at intermediate exchange rates. The spectra in the intermediate rates regime are more sensitive to the simulation parameters and provide more clues as to what kind of molecular jump model may be correct.[15,16] After carefully examining the spectra in Figure 1, one cannot miss the shoulder at about 150 ppm, and also one can see the change in the shoulder at different temperatures. The simulations depicted in Figures 3 and 4 have no shoulder. This shoulder is representative of the large angle jump process and was first noticed by Pines and co-workers in their investigation of the reorientation of benzene.[16]

Figure 5 shows the results for a 6-site jump model simulation. In the slow and fast limit, the spectra are similar to the spectra in Figures 3 and 4, fitting the experimental results well. At intermediate exchange rates, the spectra in Figure 5 are different from the spectra in Figures 3 and 4, giving rise to a shoulder on the lower shielding side of the spectra. The presence of this shoulder indicates that the 6-site jump model is more sensitive to molecular motion and is similar to ethylene on the catalyst surface. Since the spectra in Figure 5 are more sensitive to molecular motion at intermediate rotation rates, and the line shapes are similar to the experimental results, the 60° 6-site jump model is a good model for further consideration.

The simulations for a 4-site 90° jump model are shown in Figure 6. The simulated spectra not only fit the experimental line shapes at the slow and the fast limit but also fit in the intermediate rate region as well. The shoulder at 150 ppm is prominent at the 100 Hz jump rate and gradually disappears as the jump rate approaches 2 kHz. Considering all the simulations in Figures 3–6, the 6- and 4-site jump models demonstrate the most favorable comparison between the simulation and the experimental data. However, given the S/N in the experimental spectra it is difficult to distinguish between the two jump models. We have used a random jump model for all the spectra in Figure 3–6. This is only important in the case where N is 12, 36, or 4. The random jump model utilized in the simulation of Figures 3–6 implies that a spin can jump to any site with the same possibility. We also simulated the same jump process by supposing that the spin can only jump to neighboring sites. The resulting simulations are not different enough to distinguish nearest neighbor jumps from an all site model. It is important to point out that the next neighbor jump model involving 3-site exchange is essentially the same (data not shown) as that for the 6-site model. That is, we cannot distinguish between a 6-site 60° jump model and a 3-site 120° jump model.

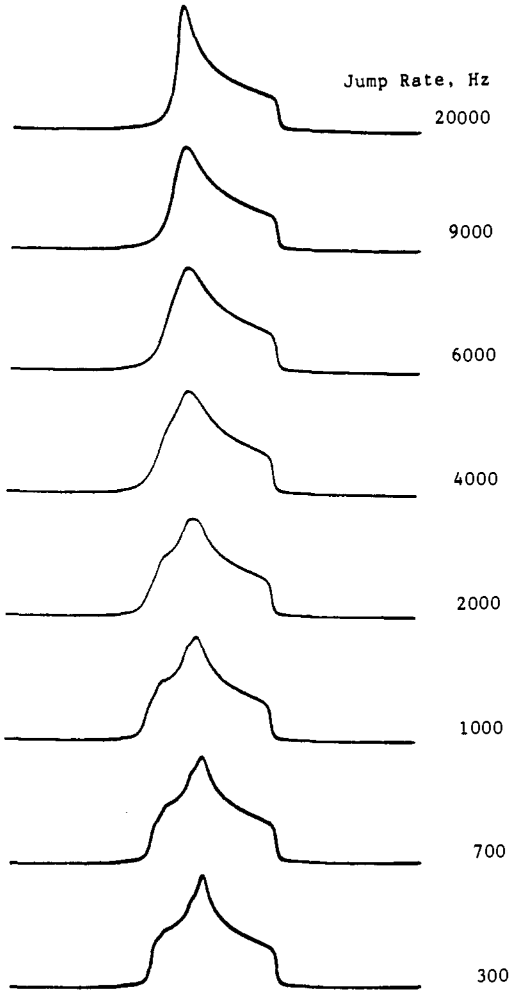

Figure 5. The simulation of 6-site 120° jumping at different exchange rates. The random model was used. The shoulders in these spectra are clearly seen around 150 ppm.

The presence of 6- and/or 4-fold axes is reflective of the type and relative number of crystallographic planes which are expressed on the silver surface. For the catalyst used here, it is not possible to say that only one kind of low index crystal face exists on the surface. It is reasonable to suppose that several low index crystal faces exist on the surface and that some higher index surface can also exist on the surface. It is believed that the main crystal faces are Ag(111) and Ag(110) on the catalyst surface, since the measured reaction rates on the single crystal Ag(111) and Ag(110) are similar to the conventional Ag catalyst.[17] Many investiga-

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(15) Baram, A.; Luz, Z.; Alexander, S. *J. Chem. Phys.* **1976**, *64*, 4321.

(16) Wemmer, D. E.; Ruben, D. J.; Pines, A. *J. Am. Chem. Soc.* **1981**, *103*, 28.

(17) Grant, R. B.; Lambert, R. M. *J. Catal.* **1985**, *92*, 364.

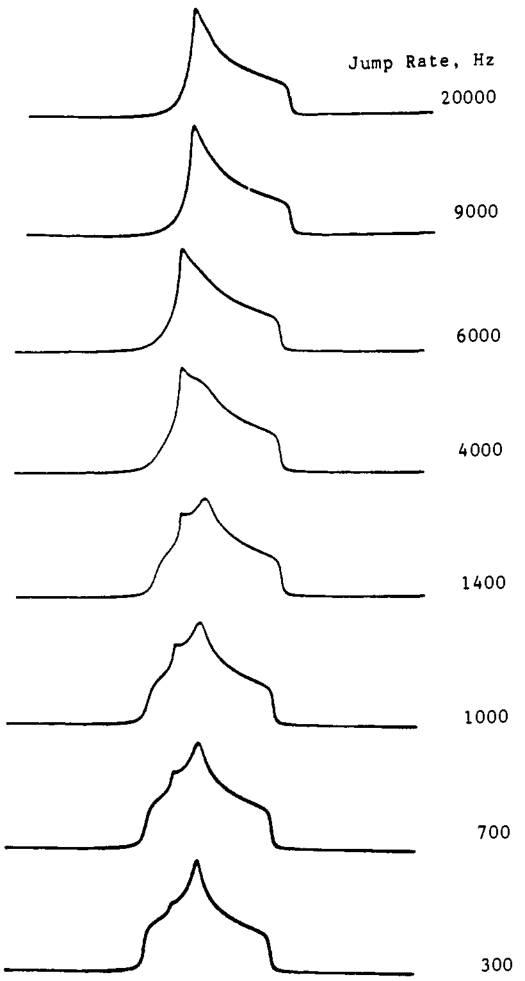
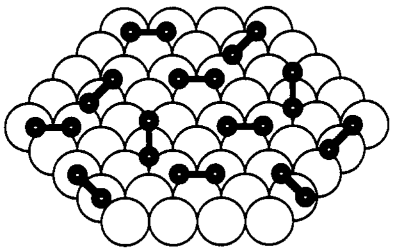


Figure 6. The simulation of 4-site 90° jumping at different exchange rates. The simulated spectra are sensitive to the jumping rates.

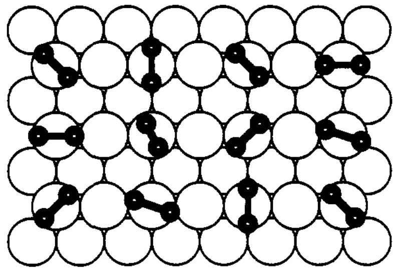


Real Structure for the Ag(111)-C2H4 overlayer

Figure 7. The space structure for the Ag(111) and C_2H_4 chemisorption.

tions[18] concerning the epoxidation reaction of ethylene or the properties of chemisorbed oxygen have been based on the Ag(111) and Ag(110) single crystals.

The adsorbed ethylene on the Ag(111) and Ag(110) faces is shown in Figures 7 and 8. As mentioned above, all experimental results suggest that ethylene directly binds to Ag through the carbon–carbon bond. The double bond of ethylene on the Ag catalyst surface was found to be 1.34 Å, identical with the value for the gas phase.[8] The Ag–Ag distance in Ag(111) and Ag(110) planes is equal to the nearest neighbor distance in the bulk Ag (R = 2.89 Å).[1,18] The C–C distance in ethylene is much shorter than the Ag–Ag distance in silver. Hence, the rotation of an ethylene molecule is always around one Ag atom. Therefore, an ethylene molecules does not need to break the bonding with the surface to reorient.



Real structure for Ag(110)-C2H4 overlayer

Figure 8. The space structure for the Ag(110) and C_2H_4 chemisorption.

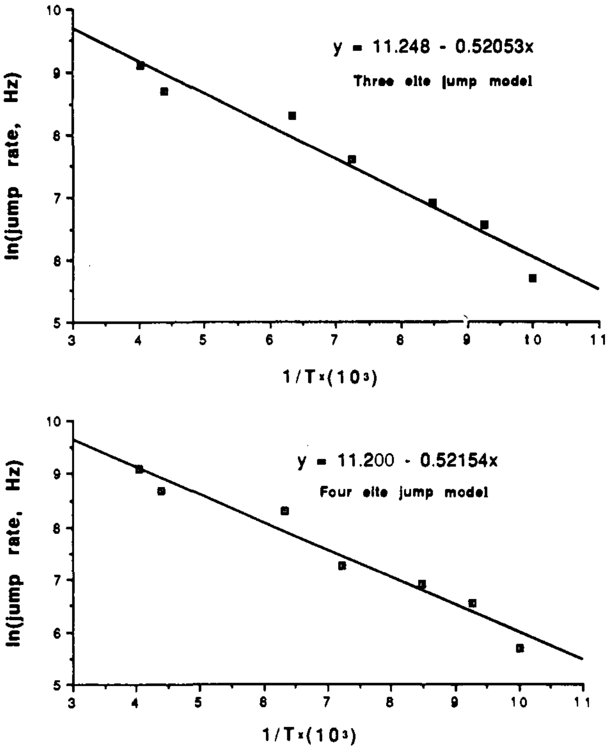


Figure 9. An activation energy plot for ethylene adsorbed on a γ-alumina supported Ag catalyst is shown. Rates were determined by comparison between experimental and simulated spectra.

It is clear that the experimental data summarized in Figure 1 cannot distinguish between a 6- or 4-site jump model. However, examination of Figures 7 and 8 demonstrates that either or both models may be representative of the motion of ethylene adsorbed to a silver surface. That is, the 4-site jump model corresponds to the rotation on the Ag(110) face, and the 6-site jump model corresponds to the rotation on the Ag(111) face. Therefore, the existence of two jump models being able to fit the observed temperature dependence of the ^{13}C powder line shape has physical meaning. That is, they both contribute significantly to the ^{13}C spectra.

By comparison of the simulated spectra for either the 6- or 4-site model and experimental spectra, we obtained the jump rates that correspond to the experimental temperatures. For instance, by comparing the simulated spectra (4-site) to the experimental spectra we found that the simulated spectrum at the jump rate of 1 kHz was similar to the experimental spectrum at −135 °C, thus we related the jump rate of 1 kHz to the experimental temperature of −135 °C. Likewise, the jump rates of 0.3, 0.7, 1.4, 4.0, and 6.0 kHz are similar to the experimental line shape at −173, −165, −155, −115, and −45 °C. The simulation error limit is approximately 20%. The log of the jump rates as a function of temperature for 6- and 4-site models is shown in Figure 9. The plots indicate a straight-line relationship, which conforms to Arrhenius behavior. From the slope of the line, the activation energy for the jumping process can be estimated. For ethylene

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[18] Carter, E. A.; Goddard, W. A., III *Surf. Sci.* **1989**, *209*, 289.

adsorbed on the Ag surface this value is found to be 4.3 ± 0.9 kJ/mol (or ~1 kcal/mol) for the 4-site model. For the 6-site model, a similar activation energy is obtained. However, due to a 20% simulation error, the estimated error for activation energy should be also approximately 20%. This low activation energy is consistent with the experimental result for adsorption of ethylene on the Ag catalyst surface, because a low heat of adsorption value has been reported on the supported Ag catalyst surface.[19,20] It is interesting to point out that Carter and Goddard[18] reached similar conclusions concerning the reorientation barrier utilizing ab initio calculations. They found that the 1-coordinate site models like the one employed here are nearly degenerate in energy with the ground state and as a result should have essentially no barrier to rotation about the Ag–C_2H_4 bond.[18]

So far the spectra simulated are the experimental data from the slow to the fast limit, that is, from −173 to −45 °C. However, the spectrum at room temperature is quite different and it is not possible to simulate these data by using the jump models described above, since those models can only yield spectra with axial symmetry in the limit of infinite rate constants. To simulate the room temperature spectrum (data not shown), the symmetry (or jumping) axis must reorient to a different angle, i.e., motion by about another axis. Owing to the barrier for desorption from the surface, it is difficult for the symmetry axis to reorient to arbitrary angles while adsorbed to a single silver atom. It is believed that ethylene on the surface of the catalyst can move in two dimensions easily at room temperature, because of the weak bonding between ethylene and the Ag surface. The translation of the ethylene symmetry axis has no effect on the motional narrowing, since the molecule still rotates around the symmetry axis, and the spectrum for this case still has axial symmetry. However, the spectrum at room temperature is nearly isotropic, indicating that the symmetry axis is reorienting. When using a two-axis rotation model to simulate the spectrum at room temperature (the rotation is around the jump axis and the jump axis rotates at different angles, e.g. a cone or discrete angles in plane), we found that we cannot simulate the spectrum. However, the line shape is narrowed with the jump axis deviating from 90° to 45° relative to the surface. It is probable that ethylene on the Ag catalyst surface is so weakly adsorbed at room temperature that the jump axis of ethylene begins to reorient to another angle at temperatures close to room temperature. When this angle becomes large enough, ethylene may move to another silver atom. Depending upon the details of the silver atom exchange, the ethylene may be rotated in such a way that the face exposed to the silver surface may be exchanged as well. The silver atom exchange will randomize the orientation of the second (or higher) jumping axis with respect to the molecular frame, giving rise to a chemical shift tensor which is nearly isotropically averaged at room temperature.

Conclusions

Ethylene on a silver catalyst is weakly adsorbed. It is found that the experimental spectra are sensitive to the molecular motion at the intermediate exchange rates, and the different jump models can be distinguished at the intermediate exchange rates. It is found that the 4- and 6-site jump models are the most suitable for the description of the motion of ethylene on the surface of the catalyst. The activation energy for the jumping process is found to be low, 4.3 kJ/mol, which is consistent with the low heat of adsorption value for ethylene on a Ag catalyst. It is concluded that the jump axis of ethylene reorients at room temperature. The present analysis demonstrates the sensitivity of the solid state NMR line shape to the microscopic details of molecular motion which can be exploited to study molecules adsorbed on surfaces.

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(19) Backx, C.; de Groot, C. P. M.; Biloen, P.; Sachtler, W. M. H. *Surf. Sci.* **1983**, *128*, 81.

(20) Anderson, K. L.; Plischke, J. K.; Vannice, M. A. *J. Catal.* **1991**, *128*, 148.