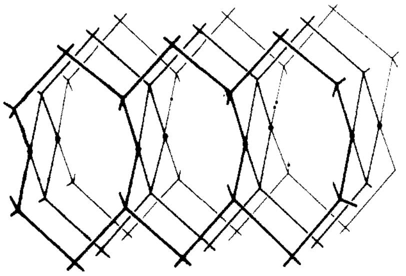

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of deriving the cubic diamond structure from **2**.

Conclusion

We hope we have demonstrated how the non-Zintl electron count of the HP LiGe structure is related to the presence of weak Ge···Ge bonding and the distorted square-planar geometry for $^2/_3$ of the Ge atoms seen in the structure. The amount of covalent interlayer bonding is small, and the layers are probably largely held together by ionic forces involving the Li^+ ions. However, such bonding is greater in the observed structure than in an alternative structure in which all Ge atoms have distorted tetrahedral geometries, for the same reasons that hypervalent (10e) AH_4 complexes adopt planar structures. We think that some of the hypothetical variants described in the last section will not remain unsynthesized for long.

Computational Appendix

All calculations are of the extended Hückel method, using the tight-binding model for extended systems. The parameters used for Ge[8] (2s, H_{ii} −16.0 eV, $\zeta = 2.16$; 2p, $H_{ii} = -9.00$ eV, $\zeta = 1.85$) and H[9] (1s, $H_{ii} = -13.6$ eV, $\zeta = 1.30$) were taken from previous work. For the calculation of properties averaged over the Brillouin zone (total energies, DOS and COOP curves) special k-point sets chosen by the method of Ramirez and Böhm[10] were used. These sets assumed tetragonal symmetry, and contained 15 points for the 3D systems and 55 points for the 2D Ge layer.

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(8) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126.
(9) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.
(10) Ramirez, R.; Böhm, M. C. *Int. J. Quantum Chem.* **1986**, *30*, 391.

Reactions of Butadiene in Zeolite Catalysts by in Situ Variable-Temperature Solid-State Nuclear Magnetic Resonance Spectrometry

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Abstract: The mechanisms by which butadiene oligomerizes in acidic zeolite catalysts leading to deactivation by pore blockage have been elucidated by using in situ ^{13}C solid-state NMR spectroscopy with magic-angle spinning (MAS). Butadiene is found to oligomerize primarily by the 1,4-addition reaction upon adsorption at its melting point (164 K). Secondary reactions of the oligomers are strongly dependent upon the properties of the zeolite. The initially formed linear product undergoes cyclization reactions to form fused rings in zeolite HY, but isolated rings are formed in the smaller channels of zeolite HZSM-5. Branching reactions and/or 1,2 enchainment result in an appreciable methyl group content in the oligomers formed in zeolite HY. These results provide insight into the mechanisms by which oxide catalysts are deactivated by pore blockage. Neither carbenium ions nor any other reactive intermediates were observed spectroscopically, presumably because such intermediates reacted with either free butadiene or the oligomers so rapidly as to preclude a detectable steady state concentration. A novel experimental procedure for in situ MAS NMR studies of chemical reactions in heterogeneous catalysis is described. This procedure is useful for adsorbates which are too reactive and/or insufficiently volatile for the recently reported CAVERN experiment.

The reactions of hydrocarbons and other adsorbates within zeolite catalysts are of great interest. Traditionally, such reactions are studied by making inferences based on the volatile product distribution or on spectroscopic data obtained following external sample treatment.[1] With the development of high resolution ^{13}C magic-angle spinning (MAS) NMR spectroscopy of solids,[2] the observation of such reactions in situ has become a realistic goal, especially if variable-temperature methods[3] are employed. Recently, this laboratory reported an in situ study of the reactions of propene on the solid-acid catalyst zeolite HY.[4] In that investigation, a novel sample preparation chamber called the CAVERN (cryogenic adsorption vessel enabling rotor nestling) was used to adsorb the olefin on the catalyst and seal the sample in an MAS rotor at temperatures sufficiently low to prevent the onset of reaction. Sealed rotors prepared in the CAVERN were then transferred to a precooled MAS NMR probe, and chemical reactions in the zeolite channels were induced by a stepwise temperature ramp. Parallel experiments with ^{13}C labels in different positions (i.e., different isotopomers of propene) showed that label scrambling did not occur and allowed the reaction mechanism to be elucidated.

Conjugated dienes such as butadiene are expected to be considerably more reactive than simple olefins such as propene and are, therefore, expected to be particularly challenging adsorbates for in situ studies of reactions on heterogeneous catalysts. Furthermore, the reactions of dienes on acidic zeolites and related

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(1) Anderson, M. W.; Klinowski, J. *Nature* **1989**, *339*, 200.
(2) For reviews of the CP/MAS NMR technique, see: (a) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 210. (b) Maciel, G. E. *Science (Washington, D. C.)* **1984**, *226*, 282.
(3) Haw, J. F. *Anal. Chem.* **1988**, *60*, 559A.
(4) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052.

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catalysts are of great practical interest as they are known to promote catalyst deactivation by the formation of coke deposits.[5]

In this contribution we report in situ ^{13}C MAS NMR studies of the reactions of butadiene-*1*-^{13}*C* and butadiene-*2*-^{13}*C* on zeolites HY and HZSM-5. These catalysts were selected on the basis of their considerable importance in the chemical industry and because it was anticipated that the large differences in channel sizes and acid site concentrations would be reflected in the structures of the oligomeric products. These expectations were borne out. The oligomerization chemistry of butadiene in acidic zeolites is generally consistent with what is known from studies of cationic polymerization in solution.[6] The formation of fused aliphatic ring systems is observed in HY, but only isolated rings are observed to form in the much smaller channels of HZSM-5. These rings are proposed to be precursors to aromatic coke molecules.

In contrast to the previous in situ study of propene on HY,[4] no reactive intermediates such as framework-stabilized incipient carbenium ions are observed in the present investigation. This result is rationalized by proposing that the high concentration of olefinic groups in both the oligomer and the reactant preclude a detectable steady state concentration of intermediate. A variation of the CAVERN experimental procedure was developed for the preparation of highly reactive samples for in situ MAS NMR studies. This procedure will also be useful for studies of nonvolatile adsorbates, a major limitation of the original CAVERN procedure.

Experimental Section

Sample Preparation. Butadiene-*1*-^{13}*C* (99.5% ^{13}C) and butadiene-*2*-^{13}*C* (99.2% ^{13}C) were obtained from MSD Isotopes. NaY zeolite (Strem), with a Si/Al ratio of 2.3, was exchanged five times with 1 M NH_4NO_3 (99.85%, Mallinckrodt) to obtain NH_4Y zeolite which was then converted to HY catalyst by a multistep activation procedure previously outlined.[4] The ammonium-exchanged form of zeolite ZSM-5, with a Si/Al ratio of 70, was obtained from Mobil Research and Development Company and activated in the same manner.

The preparation of samples for in situ variable-temperature MAS NMR studies was carried out using a modification of the CAVERN procedure which is described later in the text.

NMR Spectroscopy. All ^{13}C solid-state NMR spectra were acquired at 25.02 MHz on a Chemagnetics M-100S spectrometer with use of magic-angle spinning (3–4 kHz) and variable-temperature methods described elsewhere.[7] Samples were spun using dry nitrogen gas obtained directly from boil off of the liquid. Other experimental details are described in the text as appropriate. Relaxation measurements were performed with use of standard methods,[8] and at least seven delay values were used to characterize each curve.

Results and Discussion

Before discussing the in situ experiments, it is appropriate to consider whether or not ex situ methods can be used to characterize the oligomerization products of butadiene formed in acidic zeolites. To test this possibility, a number of samples were prepared by adsorbing unlabeled butadiene on zeolite HY at various temperatures between 195 and 293 K. With use of Soxhlet extraction with either methylene chloride or toluene, it was impossible to isolate sufficient organic matter for characterization by gas chromatography–mass spectrometry. We then attempted to isolate the oligomeric products through a degradative procedure. Magnoux and co-workers[9] have reported an HF digestion procedure which was claimed to permit the isolation of a wide range of adsorbed hydrocarbons by the destruction of the zeolite matrix. It was reported that even olefins could be recovered unaltered by this procedure. Several attempts were made to apply this procedure for the characterization of the reaction products of butadiene formed by adsorption on HY. Through refinement of the HF degradation procedure, we were eventually able to isolate an appreciable amount of the organic material adsorbed on the catalyst as butadiene. We attempted to characterize these isolates by ^{1}H and ^{13}C solution-state NMR spectroscopy and gas chromatography–mass spectrometry. These experiments revealed that the isolates were extremely complex aliphatic and cycloaliphatic low polymers in the range of hexamer to decamer. Neither the NMR spectra nor the total ion trace showed any fine structure (spectra not shown). Since the in situ solid-state NMR experiments (vide infra) revealed that the oligomeric product contained a substantial amount of olefinic functionality whereas the solution spectra of the HF isolates showed negligible olefinic or aromatic functionality, it was apparent that the oligomers were far too reactive for isolation and ex situ identification. The following discussion therefore deals exclusively with in situ spectroscopy.

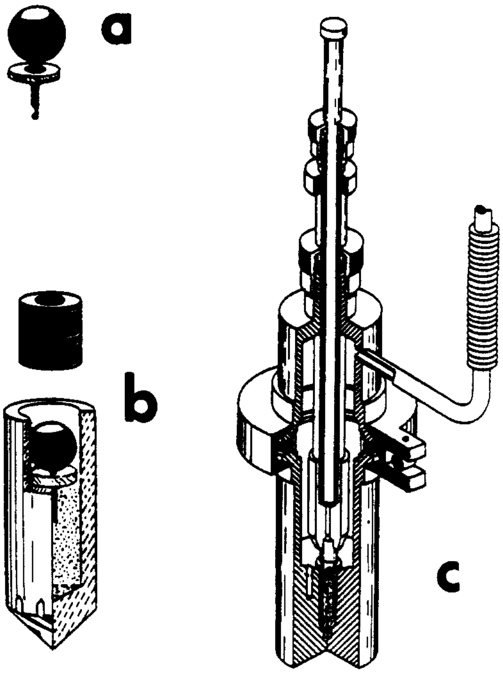

Figure 1. Diagram of the equipment used to prepare samples for in situ MAS NMR studies. (a) View of the sealed ampule and washer used for adsorbing highly reactive and/or nonvolatile compounds onto catalysts at cryogenic temperatures. (b) View of the ampule and washer loaded on top of the catalyst bed in an MAS rotor. (c) The CAVERN apparatus, in which the rotor is capped (crushing the ampule) at a temperature below the adsorbate's freezing point.

We attempted to use the recently reported CAVERN apparatus (Figure 1c) for the preparation of samples for in situ variable-temperature ^{13}C MAS NMR. ^{13}C-labeled butadiene was adsorbed into a rotor packed with activated zeolite HY at a temperature of 193 K, then the rotor was sealed and immediately transferred to the precooled MAS NMR probe. In each of several attempts it was found that the butadiene had reacted appreciably before the sample reached the NMR instrument. Several attempts were made to perform adsorptions at lower temperatures, but these failed due to the low vapor pressure of butadiene (e.g., 1 Torr at 170 K).

Clearly another method had to be developed for adsorbing butadiene on zeolites so as to preclude reaction until spectral acquisition commenced. This was accomplished by a modification of the CAVERN procedure shown in Figure 1a–c. Samples of 0.3 mmol of labeled butadiene were liquefied and sealed in small (5 mm) spherical glass ampules with use of standard vacuum line techniques. The sealed ampule and a Kel-F washer (Figure 1a) were loaded on top of a bed of 0.25 g of activated catalyst packed in a Kel-F MAS NMR rotor (Figure 1b) which was then loaded into the CAVERN apparatus (Figure 1c) as described previously. The above operations were performed in a glovebox. As before, the CAVERN was attached to a vacuum line, evacuated, and

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(5) Langner, B. E.; Meyer, S. In *Proceedings of the International Symposium on Catalyst Deactivation*; Delmon, B., Froment, G. F.; Eds.; Elsevier Scientific: New York, 1980; pp 91–102.

(6) Kennedy, J. P. *Cationic Polymerization of Olefins: A Critical Inventory*; Wiley-Interscience: New York, 1975; pp 154–164.

(7) Haw, J. F.; Campbell, G. C.; Crosby, R. C. *Anal. Chem.* **1986**, *58*, 3152.

(8) Sullivan, M. J.; Maciel, G. E. *Anal. Chem.* **1982**, *54*, 1615.

(9) Magnoux, P.; Roger, P.; Canaff, C.; Fouche, V.; Gnep, N. S.; Guisnet, M. In *Proceedings of the Fourth International Symposium on Catalyst Deactivation*; Delmon, B., Froment, G. F., Eds.; Elsevier Scientific: New York, 1987; pp 317–331.

Table I. Relaxation Data for Butadiene and Its Oligomerized Products Determined at Various Temperatures

	T_{CH} (ms)				^1H $T_{1\rho}$ (ms)				^{13}C T_1 (ms)				^1H T_1 (ms)			
	C_4H_6	olefinic	CH, CH_2	CH_3	C_4H_6	olefinic	CH, CH_2	CH_3	C_4H_6	olefinic	CH, CH_2	CH_3	C_4H_6	olefinic	CH, CH_2	CH_3
butadiene-*1*-^{13}C on HY																
193 K	0.541		0.038	0.115	20.6		12.5	13.5	60.2		625	125	217		335	226
293 K			0.031	0.114			17.4	19.6			2070	687			518	477
butadiene-*2*-^{13}C on HY																
193 K	0.458	0.036	0.032		23.0	9.2	12.9		88.4	1400	1700		302	291	336	
293 K		0.063	0.041			14.0	17.6			764	1680			445	431	
butadiene-*1*-^{13}C on HZSM-5																
173 K	0.065		0.031		13.0		7.9		153		708		87		105	
203 K	0.053		0.038		7.0		9.1		621		643		208		196	
293 K	0.087		0.037		19.0		7.0		504		368				192	
butadiene-*2*-^{13}C on HZSM-5																
173 K	0.064	0.053	0.048		12.9	9.7	10.0		219	568			97	106		
203 K	0.202	0.192	0.132		21.7	15.9	11.4		702	637	1190		278	249	272	
293 K	0.100	0.077	0.071		21.6	31.1	20.6		1434	924	992		198	190	202	

cooled—this time to a temperature well below the freezing point of butadiene (164 K). The rotor was then sealed by pushing the cap into place, crushing the glass ampule between the cap and washer in the process. The sample, consisting of a layer of solid butadiene above a bed of catalyst, was then transferred to the MAS NMR probe, which was precooled to 143 K. The fact that adsorption had not occurred could be ascertained from the spectroscopic properties, which were consistent with an organic solid. Adsorption was initiated by slowly raising the sample through the melting point of butadiene while obtaining ^{13}C spectra with magic-angle spinning. Melting with coincident adsorption was signaled by dramatic changes in the spectroscopic properties of butadiene and the onset of chemical reaction.

Four in situ experiments were performed with use of the procedure described above: each of the two ^{13}C isotopomers was reacted on each of zeolites HY and HZSM-5. Essentially the same experimental protocol was used in each experiment.[10] Spectral acquisition began at 143 K and was continued at 10 K intervals all the way to 293 K. At each temperature, ^{13}C spectra of various types were obtained. Cross-polarization spectra were obtained with a 2-ms contact time, a 1-s pulse delay, and 400 scans. Interrupted-decoupling spectra were acquired with a 2-ms contact time, a 1-s pulse delay, 400 scans, and a dipolar dephasing time of 50 μs. The unreacted butadiene component was selectively observed with use of a ^{13}C 90° pulse (Bloch decay) followed by a brief delay in decoupling to further suppress small signals from olefinic carbons in the oligomer (100 scans, 2-s pulse delay). The interrupted-decoupling experiment[11] made it possible to differentiate CH and CH_2 carbons from quaternary or CH_3 carbons in the rigid oligomers—the former carbon types are suppressed by interrupted decoupling while the latter are not. For the experiments performed with zeolite HY it was also possible to obtain ^{13}C CP/MAS spectra in which the contribution from unreacted butadiene was suppressed by exploiting large differences in ^{13}C spin–lattice relaxation times (T_1) between the reactant and oligomer (vide infra). In some cases, detailed relaxation experiments were also performed. The results of these experiments are summarized in Table I. These data indicate that cross polarization spectra obtained using the conditions described above are reasonably quantitative for both the oligomer and unreacted butadiene. Other relaxation data in Table I will be referred to as appropriate in the discussion which follows.

Selected ^{13}C CP/MAS and Bloch decay/MAS spectra from the CAVERN experiment performed for butadiene-*2*-^{13}C on HY are shown in Figure 2. At temperatures below its freezing point (164 K), butadiene was difficult to detect by either experiment. As the temperature was raised above the melting point, butadiene entered the zeolite where its mobility was sufficiently anisotropic for cross polarization yet sufficiently rapid for a short ^{13}C T_1 (Table I). Oligomerization began to occur immediately after melting and the consumption of butadiene was essentially complete by the time that the sample temperature was raised to 263 K, as confirmed by the Bloch decay spectra in Figure 2.

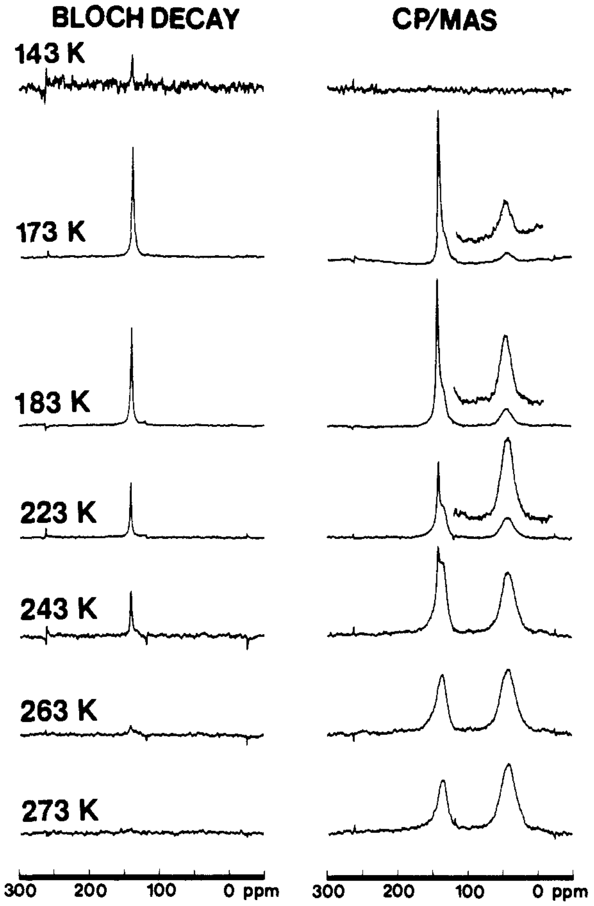

Figure 2. ^{13}C MAS NMR spectra showing butadiene-*2*-^{13}C reacting on HY catalyst as the temperature was raised from 143 K to ambient. The sample was prepared with use of a sealed ampule containing the reactive hydrocarbon and the CAVERN apparatus. Experimental conditions are described in the text.

Very early in the course of the experiment depicted in Figure 2, it was noted that there was appreciable overlap in the cross-polarization spectra between the oligomeric olefin resonance at 134 ppm and the peak at 138 ppm (unreacted butadiene-*2*-^{13}C). Since these resonances were characterized by a large difference in ^{13}C T_1, it was feasible to obtain cross-polarization spectra with the reactant peak suppressed by inverting the ^{13}C magnetization for a period of time corresponding to the null condition. The spectra so obtained were easier to interpret in terms of the structure of the oligomers. The spectra obtained with cross polarization and butadiene-peak suppression are presented in Figure 3 for both butadiene-*2*-^{13}C on HY and the analogous experiment involving

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[10] Taking the beginning of acquisition of the 143 K spectra as zero time, the same time–temperature course was used for each in situ experiment over the 16-h time period of each experiment.

[11] Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

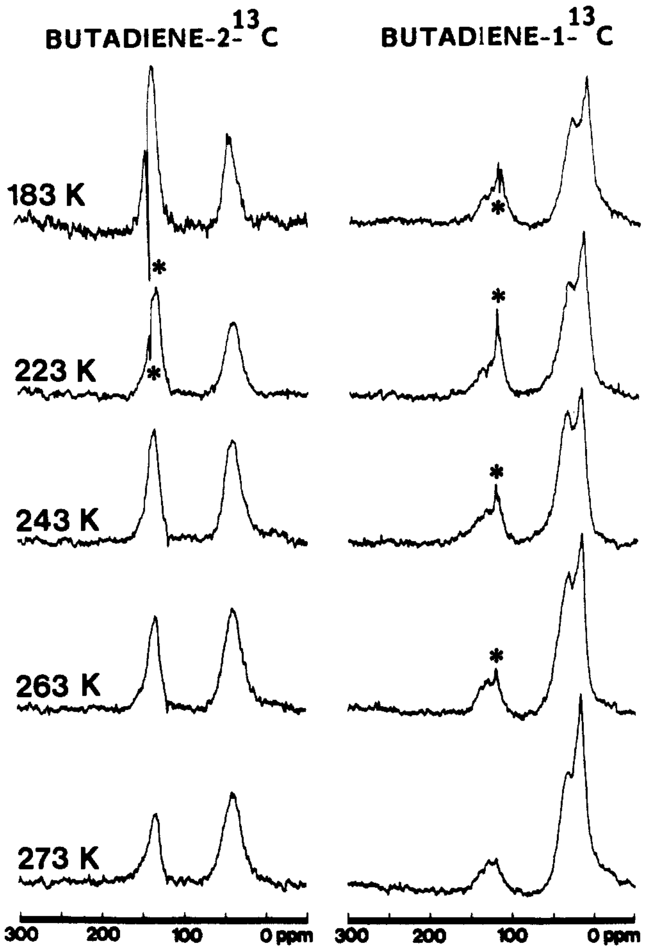


Figure 3. ^{13}C CP/MAS spectra of butadiene-*2*-^{13}*C* and butadiene-*1*-^{13}*C* reacting on zeolite HY. The spectra were acquired with suppression of the butadiene signal by inverting the carbon magnetization for a period of time corresponding to τ_{null} for the reactant (50 ms for the 2-isotopomer and 20 ms for the 1-isotopomer). An asterisk denotes residual butadiene signal.

the *1*-^{13}*C* isotopomer. For the corresponding CAVERN experiments on zeolite HZSM-5, there was generally a much smaller difference between the ^{13}C T_1s (Table I) of the reactant and product than was observed for zeolite HY, reflecting the more constrained environment in HZSM-5. Furthermore, the butadiene ^{13}C T_1s showed a more pronounced temperature dependence in the smaller pentasil zeolite, so attempts to obtain "suppression" experiments analogous to those in Figure 3 required excessive subjectivity. For those reasons, conventional ^{13}C CP/MAS spectra from the CAVERN runs on HZSM-5 are reported in Figure 4. In the discussion that follows, the spectra in Figures 2, 3, and 4 are compared and contrasted in terms of their implications for the reaction mechanisms, which are then explained in terms of the known solution-state cationic polymerization chemistry of butadiene.[6]

A cursory examination of Figures 2–4 reveals obvious differences between the spectra obtained for the two ^{13}C isotopomers—a result that rules out label scrambling. In both HY and HZSM-5, the label from butadiene-*2*-^{13}*C* is initially incorporated primarily into an oligomer olefin resonance with a chemical shift of 132–134 ppm. On the basis of interrupted-decoupling experiments and the chemical shift, as initially formed this resonance corresponds to a secondary olefin carbon (i.e., C=CHR). As the temperature increases and other reactions occur (vide infra), this resonance corresponds to an increasing concentration of tertiary olefin carbon (i.e., C=CR′R) such that the concentrations of the two types of olefinic carbon are nearly equal after the sample has been at room temperature for several hours. As the temperature is raised during CAVERN experiments on butadiene-*2*-^{13}*C*, the initially formed olefinic resonance at ca. 133 ppm decreases in relation to an aliphatic carbon resonance, which is apparently formed by secondary reactions of the original oligomeric product. This can be seen most clearly in the CAVERN experiment for the *2*-^{13}*C* isotopomer on HZSM-5 (Figure 4). The chemical shifts of the aliphatic resonances incorporating the label from the 2-isotopomer differ significantly between the two zeolites. For the oligomers formed in HY, this peak was centered at 44 ppm while the corresponding value was 36 ppm for the oligomer in HZSM-5. The mechanistic significance of this difference will be commented upon later in this contribution. By the time that the sample temperatures had been raised to 273 K, the *2*-^{13}*C* aliphatic resonance was nearly as large as the olefinic resonance for the HZSM-5 experiment (Figure 4), while it was actually larger for the analogous experiment in HY (Figures 2 and 3). On the basis of interrupted-decoupling results, the aliphatic resonances obtained from the 2-isotopomer are assigned exclusively to CH and/or CH$_2$ groups. Following storage at 253 K for several days, the intensities of the olefinic resonances were observed to have decreased further (not shown).

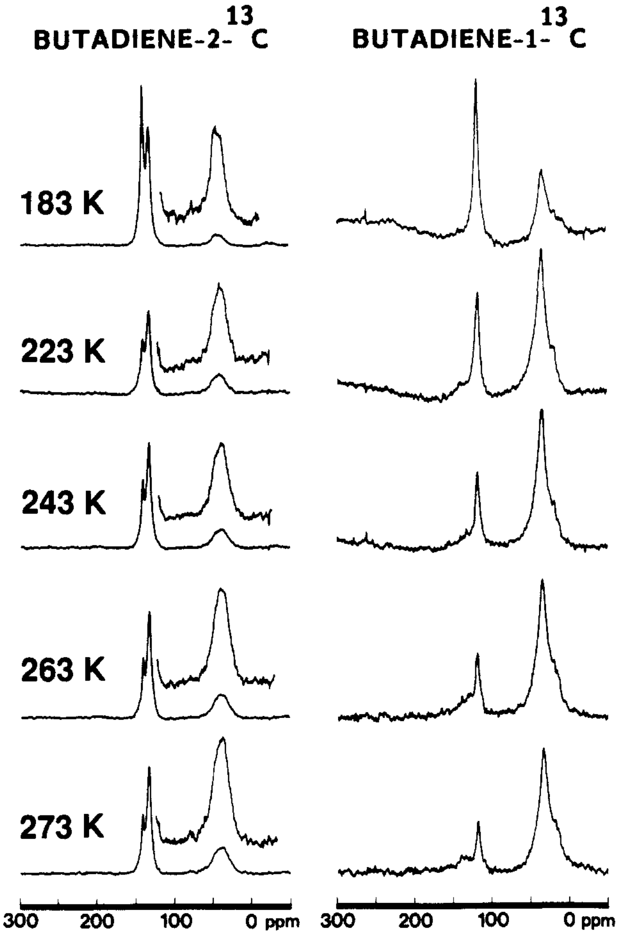


Figure 4. ^{13}C CP/MAS spectra of butadiene-*2*-^{13}*C* and butadiene-*1*-^{13}*C* reacting on HZSM-5. Butadiene peak suppression was not used (see text).

In contrast to the results obtained from the 2-isotopomer, in CAVERN experiments performed with butadiene-*1*-^{13}*C* the label was incorporated predominantly into aliphatic carbons. This was the most obvious difference between the two isotopomers. The small amount of olefinic oligomer carbon that did form from the 1-isotopomer did not survive interrupted decoupling, indicating that it was due to a mixture of C=CH$_2$ and C=CHR groups. Inspecting Figures 3 and 4, one notes a very significant difference between the aliphatic carbon resonances formed from butadiene-*1*-^{13}*C* in zeolites HY and HZSM-5, respectively. Reactions in both zeolites form a resonance centered at ca. 33 ppm that is assigned to CH and/or CH$_2$ groups on the basis of interrupted-decoupling experiments. However, the spectra for the 1-isotopomer in zeolite HY (Figure 3) show a large methyl carbon resonance

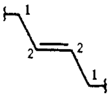
Table II. ^{13}C Solution-State Chemical Shifts of Polybutadienes[16]

repeat unit	C type	^{13}C chemical shift (ppm)
(**1**) trans-1,4	—CH$_2$—	33.2
	—CH=	130.9
(**2**) cis-1,4	—CH$_2$—	27.9
	—CH=	130.3
(**3**) 1,2	—CH$_2$—	25.4
	>CH—	44.2
	—CH=	145.3
	CH$_2$=	112.4

(which survives interrupted-decoupling) at ca. 14 ppm, which is almost completely absent in the corresponding study of HZSM-5 (Figure 4). Methyl carbon resonances are not formed in either of the experiments with butadiene-*2*-^{13}C, and quaternary aliphatic carbon resonances are not observed in any of the experiments.

Any comprehensive proposed reaction scheme for butadiene in acidic zeolites must be able to account for the chemical functionality observed, the fate of the ^{13}C labels, and the observed differences between the two zeolites, which differ greatly in both their internal dimensions and concentrations of acid sites. Such a reaction scheme must, of course, also be consistent with the known chemistry of butadiene. Butadiene is the prototypical reactant in Diels–Alder chemistry.[12] This reaction is thermally activated (E_a = 96.7 kJ/mol in the gas phase at 500 K[13]) and is neither acid nor base catalyzed. Butadiene is known to cyclodimerize to vinylcyclohexene on various oxide catalysts at temperatures of 523 K and above as a result of the concentrating effect of adsorption.[14] Although much of the spectroscopic evidence was inconsistent with Diels–Alder chemistry, the following control experiment was performed. Butadiene-*1*-^{13}C was adsorbed on NaY zeolite (which does not have strong acid sites) at room temperature; no reaction occurred. No further consideration is given to Diels–Alder chemistry in this contribution.

The cationic polymerization chemistry of butadiene in solution has been studied with a number of initiators, including Brønsted and Lewis acids.[15] The literature in this area has been reviewed by Kennedy[6] and forms the basis of the following discussion. When butadiene undergoes cationic polymerization in solution, the product is predominantly the trans-1,4 unit (**1**) with smaller but variable degrees of cis-1,4 (**2**) and 1,2 (**3**) enchainment. The carbon-numbering scheme used in all of the structures in this contribution indicates whether a particular oligomer carbon is derived from C-1 or C-2 of butadiene. The solution state ^{13}C chemical shifts of the carbons in repeat units **1**–**3** are summarized in Table II.[16] It is clear that the spectra in Figure 4 are consistent with the hypothesis that the initially formed oligomer (i.e., that at temperatures of ca. 183 K) in HZSM-5 is primarily the trans-1,4 product. With some modification (vide infra) trans-1,4 addition also accounts for many of the features of the spectra obtained for oligomers in HY (Figures 2 and 3). 1,2 addition can be ruled out as the major route in either zeolite, although the spectra are consistent with it being a minor contributor to the overall reaction pathway in zeolite HY.



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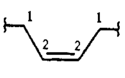

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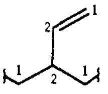

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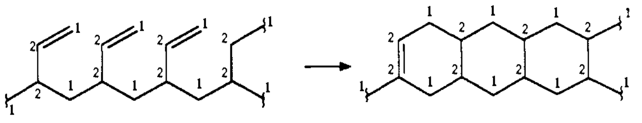
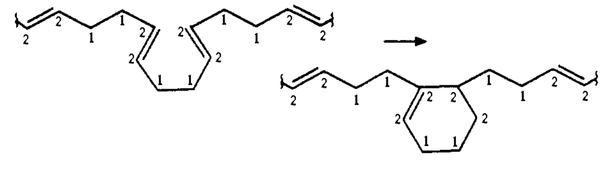
Both 1,2 and 1,4 addition yield primary oligomeric products in which one half of all of the carbons are olefinic (neglecting diene head groups). In the course of the CAVERN experiment, much of the originally formed oligomer olefin resonance is lost with the formation of aliphatic carbon resonances. Since these in situ experiments are performed on closed systems, loss of olefinic carbons can only occur through cyclization reactions that preserve the total degree of unsaturation (double bonds plus rings). Cationic polymerization in solution frequently yields products with appreciably fewer double bonds than predicted by addition reactions alone.[17] Several types of cyclization reactions are known to account for this loss of olefinic functionality. Blocks of 1,2 units can undergo the cyclization process in Scheme I, which has been termed ladder polymerization by Gaylord.[18] Trans-1,4 segments can also undergo cyclization reactions to form isolated rings (Scheme II) or fused rings (Scheme III).[6] Indeed, extensive cyclization reactions during HF digestion almost certainly occurred during the unsuccessful attempt to isolate unadulterated oligomer samples for ex situ characterization, and essentially no olefinic or aromatic functionality was found in the isolates.

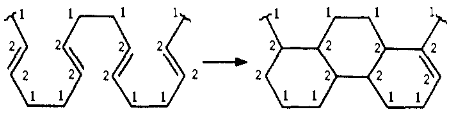
Scheme I



Scheme II



Scheme III



Do the spectra in Figures 2–4 allow the relative importance of Schemes I–III to be established for cyclization reactions of butadiene oligomers in zeolites HY and HZSM-5? The aliphatic chemical shifts differ appreciably for the oligomerization of the C-2 isotopomer in the two zeolites (35 ppm for HZSM-5 vs 44 ppm for HY). Compilations of ^{13}C solution-state spectra reveal that bridgehead carbons in fused saturated six-member rings have chemical shifts that range between 37 and 44 ppm, whereas much lower values are typical of the aliphatic ring carbons in alkyl-substituted cyclohexanes and cyclohexenes. We conclude that fused rings (Schemes I and III) predominate when butadiene oligomerizes in zeolite HY, whereas isolated rings (mechanisms such as Scheme II) form in the smaller channels of HZSM-5.[19] These results are consistent with what is known about catalyst coking at elevated temperatures.[5] Fused-ring aromatic compounds are found when Y-type zeolites are reacted with olefins at temperatures greater than ca. 150 K, but similar reactions on HZSM-5 form linear aliphatic products and alkylbenzenes.[20]

An appreciable fraction of the terminal carbons of butadiene end up as methyl groups when butadiene oligomerizes on HY, but a substantially lower fraction form in HZSM-5. Possible mechanisms for methyl group formation are now considered. The chemical shift of the methyl carbon signals in Figure 3 (14 ppm) is consistent with either the termini of linear chains or methyls on olefinic groups. The observed shift is not consistent with either methyls attached to rings (22–26 ppm) or branched alkyl groups

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(12) Wassermann, A. *Diels-Alder Reactions*; Elsevier: New York, 1965; pp 1-7.

(13) Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198.

(14) Dessau, R. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1167.

(15) Cooper, W. In *The Chemistry of Cationic Polymerization*; Plesch, P. H., Ed.; Pergamon Press: New York, 1963; pp 352-353.

(16) Conti, F.; Segre, A.; Pini, P.; Porri, L. *Polymer* **1974**, *15*, 5.

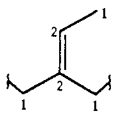
(17) Bailey, W. J. In *Vinyl and Diene Monomers*; Leonard, E. C., Ed.; Wiley-Interscience: New York, 1971; Vol. 2, p 940.

(18) (a) Gaylord, N. G.; Kossler, I.; Stolka, M.; Vodehnal, J. *J. Am. Chem. Soc.* **1963**, *85*, 641. (b) Gaylord, N. G.; Kossler, I.; Stolka, M.; Vodehnal, J. *J. Polym. Sci. Part A* **1964**, *2*, 3969.

(19) Zeolite HY has 7.4-Å diameter pores and 12.5-Å supercages. Zeolite HZSM-5 has two sets of interconnecting channels with dimensions of 5.1 × 5.5 Å (sinusoidal channels) and 5.4 × 5.6 Å (straight channels).

(20) (a) Dejaifve, P.; Vedrine, J. C.; Bolis, V.; Derouane, E. G. *J. Catal.* **1980**, *63*, 331. (b) Derouane, E. G.; Gilson, J. P.; Nagy, J. B. *Zeolites* **1982**, *2*, 42.

(18–25 ppm). The tail group of each oligomer is predicted to be a methyl group in standard cationic polymerization of butadiene, but this process alone cannot account for the high methyl content of the HY oligomer. Some of the observed intensity could be due to double bond migration in 1,2 enchainments (e.g., **4** or **5**). This is reasonable given the propensity of terminal olefins to rearrange to more stable internal olefins in acidic media. Methyl groups could also be formed by chain transfer of protonated butadienes to oligomeric olefin groups followed by deprotonation (i.e., structures **6** and **7**). The occurrence of such branching reactions in HY but not HZSM-5 is reasonable based on the larger cage and pore sizes in HY as well as the higher concentration of the acid sites that initiate reaction.



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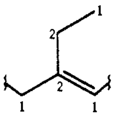

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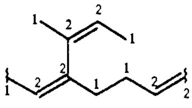

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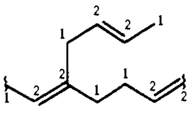

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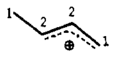
In all of the above reactions, branch points naturally occur at carbons derived from C-2 of butadiene. This observation explains why the olefinic resonance for C-2 is appreciably more intense than that for oligomer formed from the C-1 isotopomer, even at temperatures at which double bond migration should be facile. The diversity of structural units described above is consistent with the breadth of the oligomer resonances in Figures 2–4, which are much wider than those of either unreacted butadiene or the simpler oligomers formed by propene in HY.[4]

The reactions described above, 1,4 addition followed by cyclization, eventually fill the channels and deactivate the catalysts by pore blockage. This can most readily be seen by noting that a small amount of unreacted butadiene remains in zeolite HZSM-5 at temperatures far higher than that required for most of it to react (Figure 4). Indeed, this unreacted butadiene persisted after many days of storage at 253 K (not shown). The relaxation data in Table I indicate that the butadiene is in a rigid environment (e.g., short cross-polarization time constant, T_{CH}). Furthermore, the close agreement of both T_{1H} and $T_{1\rho}$ values between the oligomer resonances and those of unreacted butadiene strongly suggests proton spin diffusion between the oligomer and unreacted butadiene, a process that requires close spatial proximity. We conclude that the unreacted butadiene is trapped in the zeolite channels by channel-plugging oligomer molecules. Unreacted butadiene is more mobile in the larger HY catalyst, as suggested by its longer T_{CH} values and shorter T_{1C} values in that zeolite. Although detailed relaxation measurements were not performed for unreacted butadiene in HY over a range of temperatures, the "suppression" spectra in Figure 3 constitute single-point T_{1C} measurements. The constancy of τ_{null} in those experiments with increased temperature (which should increase diffusion) and extent of reaction (which should decrease diffusion) suggests that these two factors offset each other, and that the correlation time for butadiene remains nearly constant throughout the experiments in Figure 3. If this interpretation is correct, the diffusion of unreacted butadiene past oligomer molecules is a major determinant of the extent of reaction vs temperature in this investigation.

The question of reactive intermediates formed during the oligomerization of butadiene in acidic zeolites is now considered. Protonated butadiene species in zeolites could exist either as free resonance-stabilized allylic cations (**8**) or as incipient ions covalently bound to framework oxygens (**9**).[4,21] Although all of the reactions considered above are consistent with the same carbenium ion mechanisms invoked to rationalize solution-state cationic polymerization,[6] no reactive intermediates were observed spectroscopically in any of the four experiments depicted in Figures 2–4 or any of about a dozen other experiments performed following adsorption of either ^{13}C isotopomer at room temperature or below. The failure to observe intermediates in this study is disappointing, but perhaps not surprising. The high loading of butadiene used in these experiments in combination with the highly reactive nature of the olefinic groups in the oligomers apparently ensure a low steady-state concentration for reactive intermediates. This rationalization suggests that future attempts to observe reactive intermediates in this system should employ significantly lower butadiene loadings.



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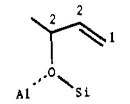

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Conclusions

The reaction of butadiene on acidic zeolite catalysts occurs at temperatures above its melting point (164 K) by 1,4-addition with some 1,2-enchainment and/or branching in HY. Cyclization reactions to form fused rings in HY but isolated rings in HZSM-5 consume much of the olefinic functionality as the reaction temperature is increased to ambient. These reactions lead to channel blockage and may be the genesis of the ring structures of aromatic coke molecules which deactivate zeolites during operation at higher temperatures.

Repeated attempts to isolate unchanged the oligomeric products for ex situ characterization with use of an HF digestion procedure were unsuccessful due to the high reactivity of the oligomers. Sample preparation techniques for variable-temperature MAS NMR were developed, which made possible the study of the oligomerization reactions in situ. No reactive intermediates were observed in this study, presumably because of the high loading of butadiene and the highly reactive nature of the oligomer.

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Registry No. Butadiene, 106-99-0.

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(21) Aronson, M. T.; Gorte, R. J.; Farneth, W. E.; White, D. *J. Am. Chem. Soc.* **1989**, *111*, 840.