Toward a Systematic Chemistry of Organic Reactions in Zeolites: In Situ NMR Studies of Ketones

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Abstract: The reactions of acetone and cyclopentanone on a variety of zeolites with different acidities and pore sizes were investigated in detail by both in situ ^{13}C solid-state NMR and ex situ methods following extraction. The overall reaction sequence was acid catalyzed aldol condensations followed by secondary reactions such as double bond migration, hydrogen transfer, and cracking, especially in the more acidic zeolites. The formation of reactive complexes between the ketones and the Bronsted acid sites of the zeolites is implicated as a precursor to condensations at low temperature. The strength of complex formation was reflected in the extent of proton transfer to the ketone, and this was mapped into significant ^{13}C isotropic chemical shift changes. These are interpreted quantitatively as a measure of the effective acidity of the zeolitic environment under actual reaction conditions using a procedure proposed by Farcasiu and co-workers [*J. Catal.* **1992,** *134,* 118]. The order of activity for aldol condensations of acetone on the various zeolites (HZSM-5 > HY > HX > NaX, CsX > CsY, CsZSM-5) is in complete agreement with this in situ measurement of acidity. The zeolites studied here were not superacids at 298 K. Free carbenium ions or hydroxycarbenium ions did not form at 298 K as long-lived intermediates from the ketones studied, even at low loadings. The aldol products obtained from acetone and cyclopentanone were generally in agreement with solution chemistry with the exception that shape selectivity was evident in the formation of trindane from cyclopentanone on large pore but not on medium pore zeolites. Cyclohexanone formed products analogous to those of cyclopentanone. The in situ NMR experiments were effective guides to the design of zeolite-based syntheses of aldol products of cyclopentanone using either sealed glass tube or refluxing solvent protocols. The overall results of this investigation suggest the emergence of a physical organic pedagogy that will systematize synthetic reactions using zeolites. Such a methodology would be important in the development of zeolite-based procedures as alternatives to existing routes to fine chemicals that also produce corrosive liquid or metal salt wastes.

Introduction

The reactions of adsorbates on zeolites are of increasing interest. Although these catalysts are most commonly discussed in the context of chemical technologies such as refining,[1] a shift in emphasis to the development of zeolite-based syntheses, either catalytic or stoichiometric, as replacements for existing procedures in the manufacture of fine chemicals may be in progress. This would be motivated by the opportunity to reduce the generation of corrosive or toxic liquids and salts, which present disposal problems, as well as the possibility of increased selectivity with zeolitic reagents. Hölderich has reviewed the use of zeolites in organic synthesis.[2,3] In other recent reviews, Weitkamp has suggested that zeolites could be viewed as reaction vessels with appropriate molecular dimensions and thus act as a template, directing synthetic reactions to the desired products.[4,5] Shape selectivity in zeolites can be manifested in terms of size constraints in the reactants, transition states, or products. Reactivity could in principle be tuned by the choice of cation or framework to tailor acidity, basicity, or redox properties. Selectivity can be further tuned by the presence of coadsorbates or the choice of

solvent.[6] Furthermore, the affinity of zeolites for some adsorbates means that effective concentrations of reactants different from those in the solution phase could be exploited synthetically.

In spite of the arguments summarized above, the mainstream synthetic community has been slow to investigate the use of molecular sieves for any purpose other than separation and purification, although there have been exceptions.[7–13] There are at least two reasons for this: First, the pore size of common zeolites and related materials is smaller than that of many synthetic targets. Recently, workers at Mobil have announced the discovery of the MCM-41 family of aluminosilicates.[14,15] These mesoporous materials have been prepared with uniform channel diameters ranging from several nanometers to perhaps 10 nm or more, depending on the composition of the micellar phase used in the preparation. The availability of mesoporous zeolites would remove the first obstacle.

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A second obstacle seems to be a relative lack of experience with zeolites as reaction media, or alternatively the ability to transfer physical organic concepts of reactivity from the solution state to the intrazeolitic state. In a recent study of carbon–carbon bond formation from methyl halides on alkali metal exchanged zeolites, we reported reactivity trends consistent with the basicity or nucleophilicity of the zeolite framework and the stability of the halide leaving group.[16] The parallels to solution chemistry prompted us to conclude that a predictive chemistry of organic adsorbates on zeolites is a realistic goal. Using methods previously developed for in situ solid-state NMR studies of catalytic reaction mechanisms, we have set out to establish a physical organic chemistry of zeolites as a guide to further progress in the use of zeolites in synthesis.

In this contribution, we report a detailed investigation of the reactions of acetone and simple cyclic ketones on a variety of zeolites with different pore sizes and greatly differing acidities. These reactants were selected because of the primacy of the carbonyl group in many simple transformations. We show that a wide range of activity and some degree of selectivity for various aldol products and secondary reactions can be achieved by the appropriate choice of acidity and pore size. The starting ketones and several aldol products form adsorption complexes with the acid sites of the zeolites. Complete proton transfer to form stable long-lived cations was not observed, but formation of the adsorption complexes resulted in ^{13}C chemical shift changes qualitatively similar to the protonation shifts of the same species in the acidic solutions. *The magnitude of these shifts was quantified in terms of a measure of effective acidity under actual reaction conditions, and this measure correlated with the order of activity of the various catalysts studied.*

As a secondary objective, the results of the in situ NMR experiments were applied directly in the design of synthetic preparations of aldol products from cyclopentanone using either sealed glass reaction tubes or refluxing solvent conditions. Depending on the choice of reaction conditions, either the α, β-unsaturated dimer or the aromatic compound trindane could be obtained in good yield.

Experimental Section

Catalyst Preparation. Zeolite NaX (Si/Al = 1.2) was obtained from Strem Chemicals. Zeolites HZSM-5 (Si/Al = 19) and NH₄Y (Si/Al = 2.5) were obtained from UOP Corp. CsCl and NH₄Cl were obtained from Aldrich. To prepare the Cs form of the zeolites, they were first exchanged to the ammonium cationic form to facilitate introduction of the larger Cs cation. The detailed multistep exchange procedure and elemental analysis results are reported previously.[16] Typically, catalysts were activated at 673 K by a procedure described elsewhere[17] and were used within 1 day of activation. For zeolites CsX and HX, the highest activation temperature was lowered to 623 K to avoid possible loss of crystallinity. No change in activity was observed when the catalyst was activated at 623 K instead of 673 K as measured by in situ reactions of acetone and cyclopentanone.

Reagents. Acetone-2-[13]C (99% [13]C), acetone-*1,3*-[13]C₂ (99% [13]C), acetic-*1*-^{13}C acid (99% [13]C), and cyclopentanone-*1*-[13]C (99% [13]C) were obtained from Cambridge Isotope. Acetone-*1,2,3*-[13]C₃ (99% [13]C) and isobutylene-2-[13]C (99% [13]C) were obtained from Isotech. All of these compounds were purified via several freeze–pump–thaw cycles. Diacetone alcohol (99%), mesityl oxide (98%), phorone (97%), isophorone (97%), 2,4-pentanedione (99+%), cyclopentanone (99+%), cyclohexanone (99.8%), toluene (99+%), *p*-xylene (99%), and mesitylene (99%) were obtained from Aldrich. Molecular sieve (type 3 A, 8–12 mesh beads) was obtained from EM Science.

Sample Preparation for In Situ MAS NMR. The experimental procedure for sample preparation using standard CAVERN devices is described elsewhere.[18] The samples were evacuated to pressures less

than 5×10^{-5} Torr. Typically, adsorptions were done at room temperature using loadings of 1.0–2.0 equiv of adsorbate per acid site. This experimental protocol was followed in preparing samples for the following experiments: acetone-2-^{13}C on HZSM-5, HY, CsY, HX, CsX, NaX, and CsZSM-5; acetone-*1,3*-[13]C₂ on HZSM-5, HY, and CsX; acetone-*1,2,3*-[13]C₃ on HZSM-5 and HY; acetic-*1*-^{13}C acid on HZSM-5 and HY; isobutylene-2-^{13}C on HZSM-5; cyclopentanone-*1*-^{13}C on HZSM-5, HX, and CsX. For the data in Figure 2 and Table 1, samples with loadings ranging from 0.1 to 1.0 equiv of adsobate per acid site were prepared using special shallow bed CAVERN devices[19] to ensure a homogeneous distribution of adsorbates on zeolites. Typically, 0.20–0.30 g of weighed zeolite was loaded into a shallow bed CAVERN and activated in vacuo. Adsorptions were done at room temperature. Reagents with low vapor pressures, such as mesityl oxide and isophorone, were prepared by first loading 25–35 μL of the compound into a glass bulb using a syringe.[20] The reactant was then purified several times by freeze–pump–thaw cycles. The bulb was sealed, taken into the glovebox, and set on top of the catalyst bed in a zirconia rotor. The rotor was placed in a standard CAVERN device, evacuated, and then capped in a manner that crushed the bulb between the cap and the catalyst bed. The samples requiring coadsorption of water were prepared following procedures described elsewhere.[18]

NMR Spectroscopy. In situ ^{13}C solid-state NMR experiments were performed with magic angle spinning (MAS) on either an extensively modified Chemagnetics CMC-200 spectrometer operating at 50.06 MHz or a Chemagnetics CMX-360 spectrometer operating at 90.46 MHz. Hexamethylbenzene (17.4 ppm) was used as an external chemical shift standard, and all chemical shifts are reported relative to TMS. Standard Chemagnetics pencil probes equipped with variable-temperature accessories were used to spin zirconia rotors at 3.5–4 kHz. Spectra were typically acquired over a temperature range of 298–523 K, although low-temperature protocols were occasionally used to permit the reactions of acetone to be studied beginning at 213 K. The following ^{13}C NMR experiments were performed: cross polarization[21] (CP), contact time = 2 ms, pulse delay = 1 s, 400 transients; CP with interrupted decoupling,[22] contact time = 2 ms, pulse delay = 1 s, 400 transients, dipolar dephasing time of 50 μs; single-pulse excitation with decoupling (Bloch decay), pulse delay = 10 s; 100 transients. [13]C T_1 measurements showed that adsorbed species had [13]C T_1 values less than 2 s, therefore a repetition delay of 10 s was used throughout the single-pulse excitation experiments to ensure that they were quantitative. Except where explicitly stated otherwise, all spectra reported here are Bloch decay spectra.

The data reported in Figure 2 were acquired using cross polarization to emphasize the signals from the adsorption complex. Between 2000 and 4000 transients were averaged so that the signal-to-noise ratio was great enough to allow the measurement of the chemical shifts within an uncertainty of 1 ppm. For samples without ^{13}C enrichment, typically 30 000 transients were obtained using cross polarization. In order to obtain qualitative information on the chemical shift anisotropies for selected adsorbed species, cross-polarization spectra were acquired at spinning speeds sufficiently slow to provide at least two orders of spinning sidebands.

Solution-state ^{13}C and ^{1}H NMR spectra of extracted products were acquired using a Varian XL-200 spectrometer.

Synthetic Procedures and ex Situ Identification. Two general synthetic protocols were used. In the first protocol, 1.0–2.0 g of catalyst was activated in vacuo in a Pyrex tube, 2.2 cm in outer diameter by 19 cm in length with a wall thickness of 0.22 cm. Approximately 1.0–4.0 g of reactant was loaded into the tube using standard vacuum line techniques. The sample was then isolated from the vacuum line, heated to a desired temperature determined by reference to the appropriate in situ ^{13}C NMR study, and maintained at that temperature for 0.5 h. After the sample cooled to room temperature, the glass tube was opened, and the products were extracted several times using toluene. This same protocol was used for ex situ identification of reaction products, although in such cases the amounts of catalyst and reactant were selected in order to closely mimic the in situ NMR experimental conditions.

Refluxing solvent conditions were used in the second synthetic protocol. Typically 2.5–8.0 g of activated zeolite and 10–20 g of dry 3A molecular

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Scheme 1.   General Features of the Aldol Reaction Sequence Observed in Situ for Acetone on Zeolites[a]

1

2: Diacetone Alcohol

3: Mesityl Oxide

6: Various Isomers

5: Isophorone

4: Phorone
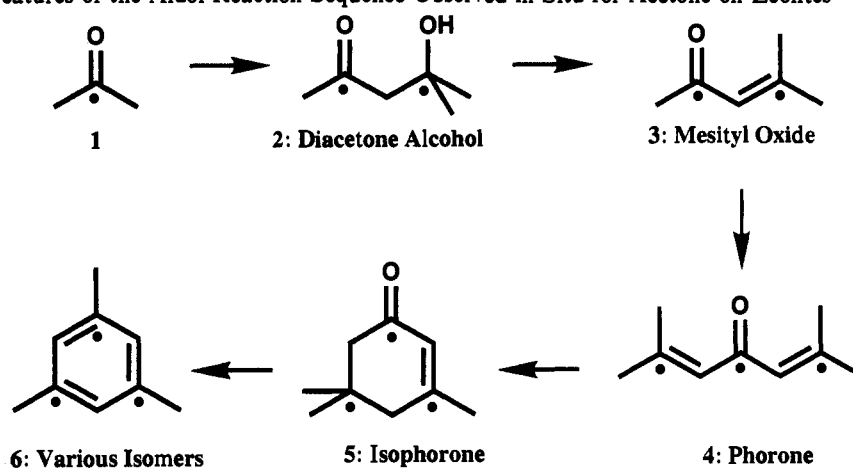
[a] Carbons derived from the carbonyl of acetone are indicated.

Scheme 2.   General Features of the Aldol Reaction Sequence Observed in Situ for Cyclopentanone on Zeolites[a]

7

8

9

12: Trindane

11

10
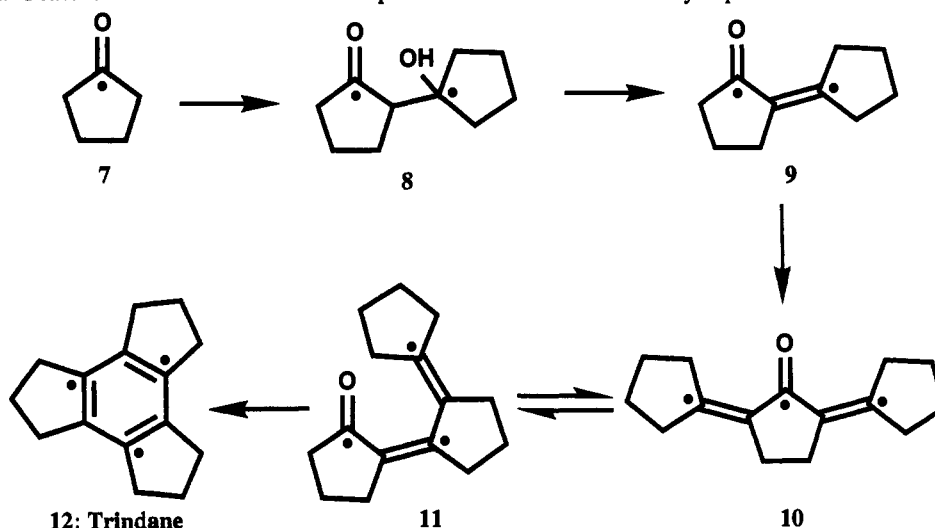
[a] Trindane formed only on the large pore zeolites. Carbons derived from the carbonyl of cyclopentanone are indicated.

sieve were transferred into a 250-mL three-necked flask in the glovebox. The flask was sealed using rubber septa, and 100 mL of freshly distilled solvent (toluene, *p*-xylene, or mesitylene) was transferred into the flask without exposure to air. To this mixture was added 10.0 g of dry cyclopentanone. The mixture was stirred under reflux for 24–70 h. After cooling to room temperature, the solution was decanted into a 250-mL round-bottomed flask. The solid residue was extracted twice with 10 mL of toluene. The combined solution was filtered to remove solid residue, and the solvent was evaporated under reduced pressure. In both protocols, the products were analyzed by GC, GC-MS, or quantitative solution state ^{13}C NMR. GC-MS analyses were carried out using a HP-5995 instrument with a DB-1 columm operated at 70 eV EI.

Results

Reviews of aldol condensations in acidic and basic solutions have been published elsewhere,[23,24] as have studies of gas-phase reactions of acetone on acidic or basic solid catalysts.[25–29] Several patents[30–32] and articles in the Russian literature[33,34] have described preparative reactions of aldol products using zeolites.

The ketones most thoroughly studied in the present investigation were acetone and cyclopentanone. Several experiments with cyclohexanone suggested that its chemistry was closely analogous to that of cyclopentanone. The reactions of acetone, cyclopentanone, and cyclohexanone on zeolites can be conveniently divided into aldol condensations and secondary reactions such as double bond migration, hydride transfer, and cracking. The primary reaction sequences observed in this study are organized in Schemes 1 and 2 for acetone and cyclopentanone, respectively. The structures in the schemes are annotated to designate carbons derived from carbonyls of the starting ketones in order to facilitate discussion of the in situ NMR studies of ^{13}C-labeled reagents. The extent of reaction and the selectivity for various products varied greatly, depending upon the specific zeolite and reaction conditions. For example, trindane formed from cyclopentanone in the large-pore (0.74-nm pore, 1.2-nm supercage) zeolite HX but not in the medium-pore (ca. 0.55-nm pore) HZSM-5 catalyst. Schemes 1 and 2 summarize the general features and allow specific examples to be discussed in terms of their differences. These schemes are generally consistent with the expected aldol products as seen in previous gas-phase and solution studies.[23–29]

In most cases products were identified unambiguously through the analysis of extracts by GC-MS and comparison to reference

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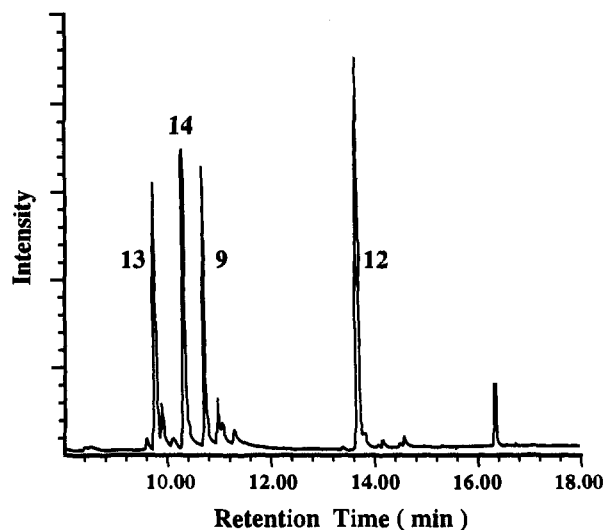
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Figure 1. Total ion chromatogram trace of the extracts of cyclopentanone on HX in a typical sealed glass tube experiment. In addition to the normal aldol condensation products **9** and **12**, secondary reaction products **13** and **14** were also formed.

spectra in data bases. In some cases these assignments were further verified by solution-state ^{13}C and ^{1}H NMR. The products identified in situ by solid state NMR were generally in excellent agreement with the ex situ analyses, suggesting that the extraction procedure did not modify the products. Assignment of the in situ spectra was also facilitated by using dipolar dephasing experiments[22] and/or by recording spectra of authentic samples of various products loaded into the zeolites under similar conditions.

Secondary Reactions. In addition to aldol condensations, several secondary reactions occurred on the more acidic catalysts or at higher temperatures and longer reaction times. The GC-MS total ion chromatogram trace in Figure 1 illustrates two such reactions. When cyclopentanone was heated for 0.5 h on zeolite HX at 453 K, three dimeric products were observed. One was the aldol product **9**, while the others were **13**, the result of reduction
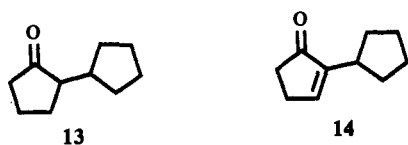
by protonation and hydride transfer, and **14**, the result of double bond migration. In the more acidic zeolites HZSM-5 and HY, cracking of primary aldol products and oligomerization and further cracking of the resulting olefins were observed at higher temperatures. On HY, for example, mesityl oxide cracked to acetic acid and isobutylene, and the latter further reacted to form the thermodynamically stable cracking product isobutane as well as aromatics. CO_2 also formed from acetone at high temperatures, probably by the successive cracking of phorone.

Adsorption Complexes and Acidity Shifts. A dominant characteristic of the in situ ^{13}C NMR experiments was the observation of large downfield shifts for selected carbons apparently due to complex formation with partial proton transfer from the Bronsted acid sites to the basic oxygen of the ketones. The related phenomenon of protonation shifts has been well characterized in solution[35-39] and is illustrated in Scheme 3.

Note that protonation of α,β-unsaturated ketones such as mesityl oxide is expected to produce appreciable downfield ^{13}C

shifts for both the carbonyl and β carbon, but the α-carbon shift is insensitive to protonation.[38,39] This effect can be seen in Tables 1 and 2. Table 1 reports ^{13}C chemical shifts for the carbonyl, C_α, and C_β of mesityl oxide in various zeolites and reaction conditions in this study. Table 2 reports the ^{13}C chemical shifts for the carbonyl and C_β of **9** in zeolites HZSM-5, HX, and CsX. The chemical shift of C_β (and to a lesser extent that of the carbonyl) is extremely sensitive to the acidity of the various zeolites *under the actual reaction conditions used in this study.*

Recently, Farcasiu and co-workers discussed the limitations of the Hammett acidity function which is commonly used to quantify acidity for both liquid and solid catalysts. Farcasiu and his colleagues proposed an alternate measurement scheme based on the ^{13}C chemical shifts of mesityl oxide and back comparison of these shifts to measurements in sulfuric acid and other solutions.[38,39] *The serendipitous formation of a "molecular pH meter" as an early aldol product in the reactions of acetone allows us to quantify the acidities of the various zeolites employed in this study under actual reaction conditions in the context of the proposal of Farcasiu and co-workers.* ^{13}C chemical shifts observed by those workers for mesityl oxide in various solutions are also reported in Table 1. Comparing the ^{13}C chemical shifts in that table suggests the conclusion that even the most acidic zeolite studied, HZSM-5, is only as strong an acid (at ca. 298 K) as a solution of ca. 70% sulfuric acid. Zeolites are commonly believed to be superacids based on catalytic reactions at high temperatures that are analogous to well-characterized reactions in superacid solutions at low temperatures. This view, at least for the majority of acid sites in HZSM-5 and HY, is clearly wrong, although the data in Table 1 cannot rule out the possibility that a small percentage of the total Bronsted sites are superacidic even at low temperatures.

The order of acidity for the zeolites suggested by Table 1 is in excellent agreement with the order of activity for the aldol condensations of acetone seen in the in situ NMR studies from which those data were measured. The NaX and CsX zeolites show slightly larger shifts than those observed for the weakest catalysts, CsY and CsZSM-5. It is impossible to fully exchange all of the protons in X-type zeolites; for example, the CsX sample contained 28% protons.[16] The small acidity shifts as well as the activity of these catalysts apparently reflect residual weak Bronsted sites. The order of acidity HZSM-5 > HY > HX implied in Table 1 has been explained previously in terms of the effect of the Si/Al ratio on the number of isolated acid sites and intrinsic differences due to the geometry of atoms embedded in the ZSM-5 vs faujasite framework.[1,41]

The formation of adsorption complexes was also evident in the ^{13}C isotropic chemical shifts of acetone, especially at low loadings and low temperatures where chemical exchange averaging was less important. The ^{13}C chemical shift of acetone is 249 ppm[42,43] in superacidic solutions and ca. 244 ppm in 100% sulfuric acid;[37] in HZSM-5 it was only 224 ppm, even at the lowest loading studied (0.1 equiv). This chemical shift, midway between the value in CDCl$_3$ (205 ppm) and that observed in very strong acid and superacid solutions, is again consistent with our view that the standard Bronsted sites in zeolites are not equivalent to superacids in their strength at low temperatures.

It is generally accepted that most of the acid sites in HZSM-5 are equivalent to each other in terms of acid strength, whereas a gradation in strength exists for most HY samples. This is clearly reflected in the NMR titrations with acetone reported in Figure 2. The chemical shift of the adsorption complex of acetone on

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Scheme 3. Resonance Structures Rationalizing the ^{13}C Shifts Observed for Ketones and α,β- Unsaturated Ketones in Acidic Zeolites
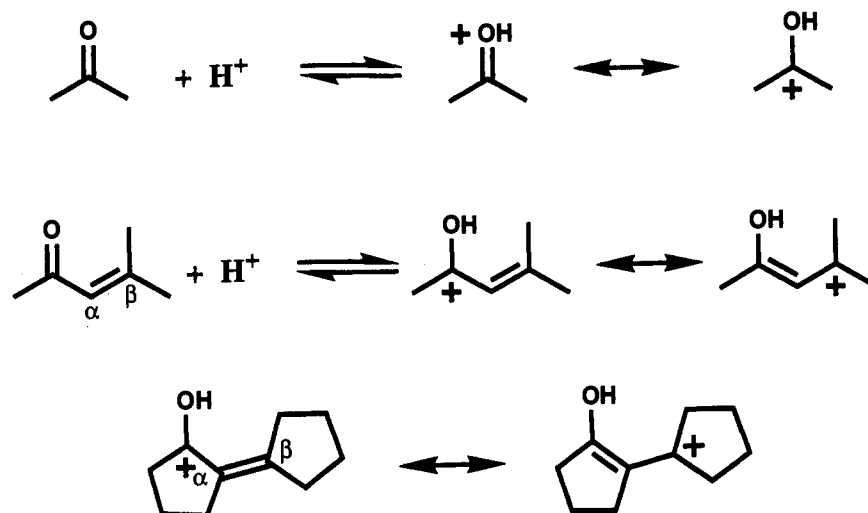
Table 1. ^{13}C Isotropic Chemical Shifts of Mesityl Oxide in Various Media at 298 K

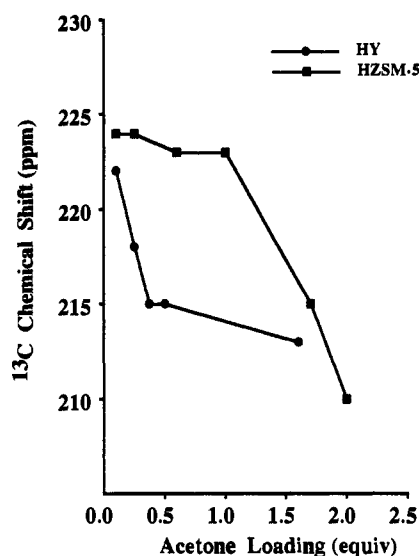| media	$H_0{}^b$	acetone loading (equiv)^c	^{13}C chemical shift^a			ref
			carbonyl	C_α	C_β	
100.0% H$_2$SO$_4$	-12.0		210	122	203	38
70.2% H$_2$SO$_4$	-5.96		211	122	191	38
HZSM-5		0.25	211	122	190	this study
HZSM-5		2.0	210	122	188	this study
HY		0.1	210		188	this study
62.5% H$_2$SO$_4$	-4.90		211	122	183	38
HY		1.2	210	123	175	this study
Cl$_2$CHCOOH	-0.75		205	124	163	38
HX		0.50	207	123	162	this study
NaX		0.50	206		162	this study
CsX		0.50	205	123	162	this study
CH$_3$COOH	0.0		201	124	158	38
CsY		1.0	205		157	this study
CsZSM-5		2.0	204		157	this study
CDCl$_3$			198	124	155	40

^{a} Reported in ppm relative to TMS. ^{b} Hammett acidity value reported in ref 38. ^{c} Initial loading as a fraction of the number of Bronsted acid sites. Measurements were performed after ca. 20% conversion to mesityl oxide.

Table 2. ^{13}C Isotropic Chemical Shifts of 7 and 9 in Various Media

|	^{13}C chemical shift^a		
	cyclopentanone (7)	2-cyclopentylidenecyclopentanone (9)	
media	carbonyl	carbonyl	C_β
HZSM-5	241		
HX	231	215	165
CsX	230	207	158
CDCl$_3$	220	207	157

^{a} Reported in ppm relative to TMS. The loading dependence was not investigated for these adsorbates.

HZSM-5 remains constant as a function of loading up to a value corresponding to one acetone per acid site. At higher loadings, this value is reduced by exchange averaging. The gradation of acid strength is evident in the analogous titration of HY. The chemical shift of the adsorption complex formed with 0.1 equiv of acetone was almost identical with that observed in HZSM-5; however, samples prepared with ca. 0.5 equiv of acetone gave rise to a ^{13}C resonance centered at 215 ppm. For comparison, the chemical shifts of acetone at relatively low loadings (typically

(44) Kubelková, L.; Nováková, J. *Zeolites* **1991**, *11*, 822–826.
(45) Kubelková, L.; Cejka, J.; Nováková, J. *Zeolites* **1991**, *11*, 48–53.
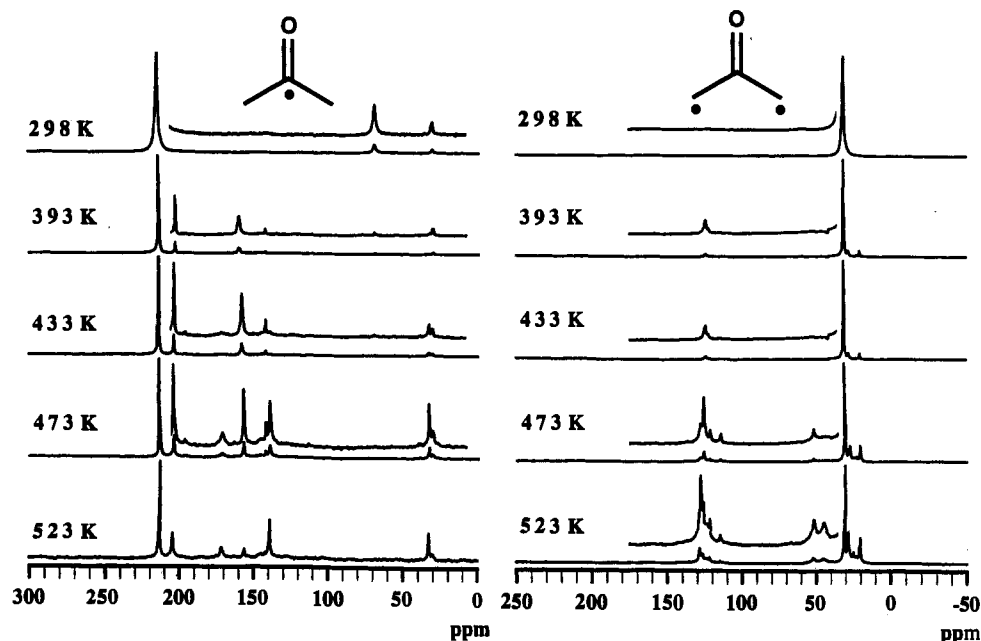(46) White, J. L.; Beck, L. W.; Haw, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 6182–6189.

Figure 2. Summary of loading-dependent ^{13}C isotropic shifts of the carbonyl carbon of the adsorption complex formed from acetone on zeolites HZSM-5 and HY.

≤ 0.5 equiv) on the other zeolites studied were the following: HX, 217 ppm; NaX, 216 ppm; CsX, 216 ppm; and CsZSM-5, 210 ppm. This order is consistent with both that seen for the chemical shifts of mesityl oxide and the activity order for aldol condensation.

Low loadings of acetone on HZSM-5 and HY produced an adsorption complex with restricted mobility as manifested in the appearance of spinning sidebands in ^{13}C MAS spectra obtained at low spinning speeds. Analogous adsorption complexes have

15
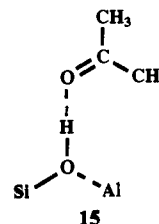
also been proposed based on infrared studies of acetone in zeolites.[44,45] We have previously invoked a structural analogy between adsorption complexes in zeolite and hydrogen-bonded gas-phase dimers formed with, for example, HCl.[46] In the absence of steric constraints, the structure of the adsorption complex (**15**)

Figure 3. In situ 50.1-MHz ^{13}C MAS NMR studies of the reactions of acetone-2-^{13}C and acetone-$1,3$-$^{13}C_2$ on zeolite CsX. Acetone was partially converted to diacetone alcohol (70 ppm in the 2-^{13}C spectra) at 298 K, which dehydrated to form mesityl oxide (205 and 162 ppm in the 2-^{13}C spectra, and 123 ppm in the 1,3-$^{13}C_2$ spectra) at 393 K. The conversion of acetone to aromatics (140 ppm in the 2-^{13}C spectra) was not complete even at 523 K.

would involve strong hydrogen bonding between the Bronsted sites and a lone pair on the oxygen of acetone. Analogous species would presumably form from mesityl oxide and other basic products and intermediates, and the extent of proton transfer from the acid sites to the ketone would be reflected in the observed ^{13}C shifts for the carbonyl and C_β resonance.

Acidity shifts were also obtained for other α,β-unsaturated aldol products (e.g., isophorone), but these were not systematically investigated.

Representative in Situ ^{13}C NMR Studies. Approximately 100 in situ MAS NMR studies were performed in the course of this investigation, and 20 or more spectra were acquired in a typical study. The results reported here are representative. The most common protocol was similar to that used in other recent reports.[16,47]

All the spectra shown of the reactions of acetone were acquired using quantitative conditions (90° ^{13}C pulse and long repetition delay). Parallel studies of acetone-2-^{13}C and acetone-$1,3$-$^{13}C_2$ are shown in each case. For cyclopentanone, the only enriched compound studied was the 1-^{13}C isotopomer, and quantitative Bloch decay spectra are paired with cross polarization (CP) spectra in the examples shown. The latter mode of excitation emphasizes immobile carbons with nearby protons. Although CP spectra can be quite nonquantitative for samples with varied proton contents and dynamics, this very property makes careful comparison of CP spectra with quantitative Bloch decay spectra a useful assignment tool.

The representative studies reported here are presented in order of increasing reactivity and decreasing ease of spectral interpretation. For some of the more reactive systems, spectral assignments might have remained tentative without ex situ identification.

Acetone on CsY or CsZSM-5. Acetone-2-^{13}C was studied on CsY and CsZSM-5, the least active of the catalysts studied (spectra not shown). A small amount of mesityl oxide formed after heating at 523 K for 30 min on either catalyst.

Acetone on CsX or NaX. The activities and selectivities of these two systems were very similar. In situ ^{13}C spectra from parallel studies of acetone-2-^{13}C and acetone-$1,3$-$^{13}C_2$ on CsX

are shown in Figure 3. A small amount of diacetone alcohol (**2**) formed at room temperature, as indicated by the resonance at 70 ppm in the acetone-2-^{13}C spectra. The α,β-unsaturated ketones **3, 4,** and **5** formed between 433 k and 473 K; each was positively identified ex situ by GC-MS. Partial conversion to aromatics (**6**) was achieved at 523 K.

Acetone on HX. This catalyst was more active than the alkali metal exchanged zeolites (spectra not shown). Formation of aromatics began at 433 K and was nearly complete after 30 min at 523 K. The conversion of isophorone (**5**) to aromatics was also studied by direct adsorption of **5** on this catalyst.

Acetone on HY. Representative results for this system are shown in Figure 4. The significantly stronger acidity of this catalyst was reflected in its activity to aldol chemistry as well as secondary reactions. Acidity shifts were quite significant for all of the ketones (Table 1 and Figure 2). A small temperature dependence of the acidity shift can clearly be seen in Figure 4. This is consistent with the expected increase in acidity with increasing temperature. Aldol condensations were the dominant chemistry through 393 K, and formation of aromatics progressed at this relatively low temperature.

Secondary reactions became very obvious when the sample was heated to 433 K, as can be most readily seen from the acetone-2-^{13}C study. Mesityl oxide cracked in the presence of water to form acetic acid (183 ppm on HY) and isobutylene which, as was previously reported,[48] immediately oligomerized and cracked to form a mixture of products including isobutane (24 ppm). Several of the observations about the secondary reactions were verified through direct study of acetic acid and isobutylene-2-^{13}C on HY (spectra not shown). CO_2 (126 ppm) also began to form at this temperature. This signal was not seen in the CP spectra (spectra not shown). The most likely source of CO_2 was cracking of phorone followed by decarboxylation of the resulting α,β-unsaturated acid. Further heating to 523 K resulted in a mixture of aromatics, C-3 to C-6 branched alkanes, CO_2, and acetic acid.

An in situ study was also performed with acetone-$1,2,3$-$^{13}C_3$ (spectra not shown). The resulting spectra were essentially composites of the parallel investigations in Figure 4.

(47) Lazo, N. D.; Murray, D. K.; Kieke, M. L.; Haw, J. F. *J. Am. Chem. Soc.* **1992,** *114,* 8552–8559.

(48) Lazo, N. D.; Richardson, B. R.; Schettler, P. D.; White, J. L.; Munson, E. J.; Haw, J. F. *J. Phys. Chem.* **1991,** *95,* 9420–9425.
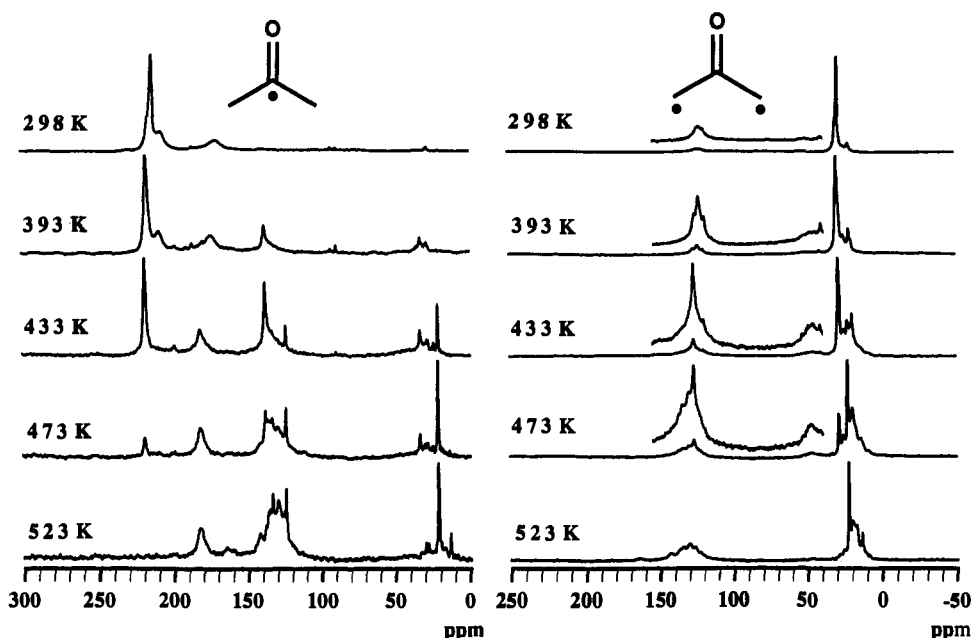
1968   *J. Am. Chem. Soc., Vol. 116, No. 5, 1994*

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Figure 4. In situ 50.1-MHz ^{13}C MAS NMR studies of the reactions of acetone-2-^{13}C and acetone-*1,3*-$^{13}C_2$ on zeolite HY. Mesityl oxide (210 and 175 ppm in the 2-^{13}C spectra, and 123 ppm in the 1,3-$^{13}C_2$ spectra) formed at 298 K. Secondary reactions at 433 K and above included the formation of acetic acid (183 ppm in the 2-^{13}C spectra), isobutane (24 ppm in the 2-^{13}C spectra), and CO_2 (126 ppm in the 2-^{13}C spectra).

Acetone on HZSM-5. This was the most thoroughly investigated system in terms of various loadings and the influence of coadsorbates. The chemistry of a number of aldol products, secondary products, and proposed intermediates was also investigated. In terms of the aldol chemistry in Scheme 1, **3** and **6** were easily extracted and identified ex situ by GC-MS, while **3**, **5**, and **6** could be identified in situ by ^{13}C MAS NMR (see Figure 5). Secondary cracking reactions similar to those observed in HY were very important in HZSM-5. The notable difference was that the yield of acetic acid (180 ppm on HZSM-5) was higher on the latter catalyst and that of CO_2 was lower. This suggests that cracking becomes a competitive reaction to aldol condensation at an earlier stage in the chemistry on HZSM-5 relative to HY.

Several experiments were also performed with acetone-*1,2,3*-$^{13}C_3$ (spectra not shown). As the reaction proceeded, the resonances broadened, suggesting that ^{13}C–^{13}C dipolar couplings were strong enough for spin diffusion[49] in this system.

The coadsorption of water was previously shown to have a significant effect on the aldol condensations of acetaldehyde.[6] In the case of acetone, this effect was much smaller. This difference might be due to the greater affinity of HZSM-5 for less polar adsorbates and/or the smaller extent of hydrate formation for acetone compared to acetaldehyde.

The acetone/HZSM-5 system displayed two spectroscopic curiosities: peaks at 85 and 95 ppm in acetone-2-^{13}C studies. These signatures did not correspond to any extractable products, and the assignment of these resonances is deferred to the discussion section.

Cyclopentanone on CsX. A representative in situ NMR study of this system is shown in Figure 6. Cyclopentanone-*1*-^{13}C (0.5 equiv, relative to the total exchangeable cations) was loaded onto the catalyst. Since 28% of the cations were protons due to the expected incomplete exchange, a significant fraction of the adsorbate could interact with weak Bronsted sites as well as possibly the weakly Lewis acidic cesium cations. These interactions were reflected in both the cross-polarization response and the presence of spinning sidebands; the study shown was performed on the high-field instrument to emphasize the latter features. At 298 K, most of the adsorbate formed an adsorption complex with

(49) Henrichs, P. M.; Linder, M. *J. Chem. Phys.* **1986**, *85*, 7077–7986.

an isotropic resonance at 230 ppm and an associated progression of spinning sidebands, while the remainder of the ketone was free as shown by a sharp peak at 221 ppm without associated sidebands.

The dimer **9** began forming at 393 K (158 and 207 ppm), and the trimer **10** started to form at 433 K (157 and 195 ppm, in close agreement with solution shifts and the expected 1:2 intensity ratio). Further heating up to 523 K resulted in nearly complete conversion to an equimolar mixture of **9** and **10** with no evidence of either the unsymmetrical trimer **11** or the aromatic compound **12**. Secondary reactions were also negligible on this zeolite reflecting the absence of strong Bronsted sites.

Cyclopentanone on HX. A representative ex situ GC-MS study of this system was discussed above (Figure 1). Figure 7 compares quantitative ^{13}C Bloch decay and CP spectra for an in situ study of the 1-^{13}C isotopomer. A natural abundance study was also performed (spectra not shown). Trindane (**11**) formed at 393 Kon HX as shown by the peak at 138 ppm in the Bloch decay spectrum. This peak was nearly absent in the CP spectra, suggesting that this species is very mobile at 393 K. Indeed, it may not even be in the zeolite under these conditions. Heating to 523 K resulted in a variety of other aromatic products due to secondary reactions.

Cyclopentanone on HZSM-5. ^{13}C spectra of cyclopentanone-*1*-^{13}C on HZSM-5 are shown in Figure 8. The yield of trindane was greatly reduced on HZSM-5, consistent with the fact that the precursor **11** cannot fit in the ca. 0.55 nm channels of this medium-pore zeolite. This presumably is an example of transition-state shape selectivity. Secondary reactions to form carboxylic acids, CO_2, and a mixture of hydrocarbons were very pronounced at 473 K and above. Ex situ analysis of extracts revealed 10-carbon aromatic compounds such as **16** and **17** in addition to **9** and **14**.

16   **17**
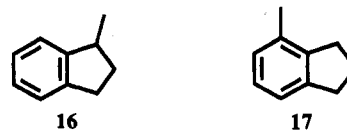
Cyclohexanone on HX. Samples of cyclohexanone with natural isotropic abundances were reacted over zeolite HX in sealed glass tubes. GC-MS analysis of the extracted products revealed the
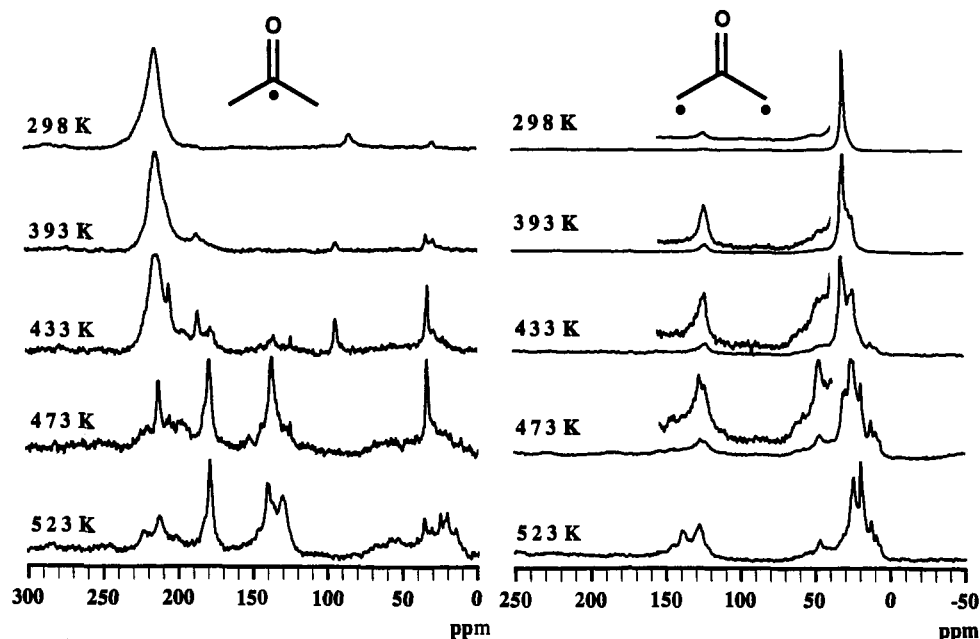
Figure 5. In situ 50.1-MHz ^{13}C MAS NMR studies of the reactions of acetone-2-^{13}C and acetone-1,3-^{13}C$_2$ on zeolite HZSM-5. Secondary reactions were signaled by the formation of large amounts of acetic acid (180 ppm in the 2-^{13}C spectra).
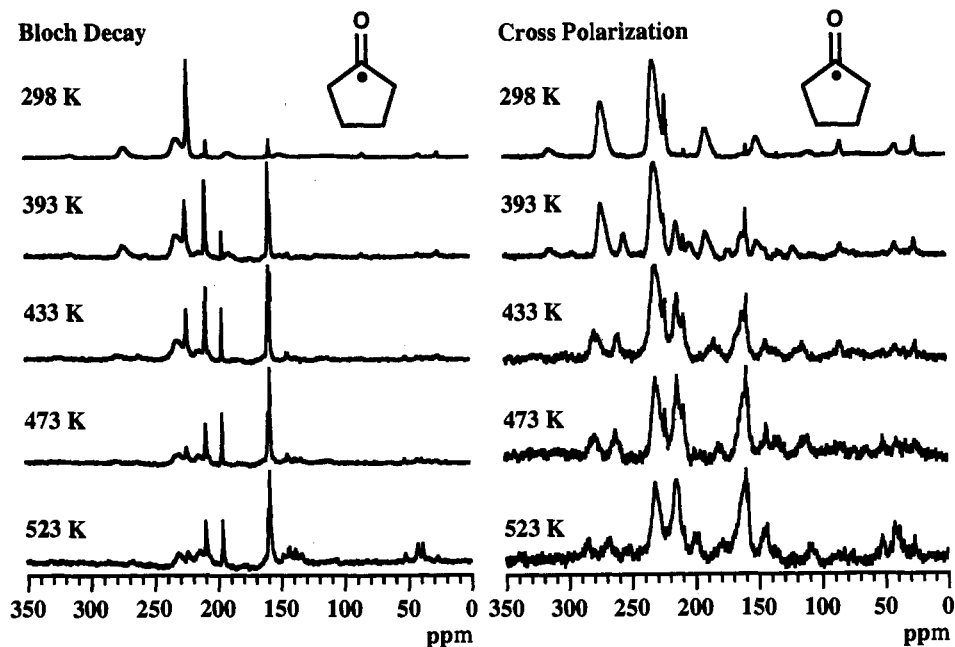

Figure 6. In situ 90.5-MHz ^{13}C MAS NMR study of the reactions of cyclopentanone-1-^{13}C on zeolite CsX. Both Bloch decay and cross polarization spectra are shown. The latter emphasizes less mobile compounds. See text for assignments.

expected aldol and secondary reaction products analogous to **9**, **12**, **13**, and **14**. Due to the lack of a commercial source of ^{13}C-labeled compounds, this reactant was not investigated any further.

Synthetic Preparations. Two general synthetic protocols were used. The conversion of cyclopentanone to trindane (**12**) was investigated with use of a sealed glass tube protocol. Although good total conversions were obtainable with this protocol, selectivity for trindane typically did not exceed 40% (cf. Figure 1). The conversion of cyclopentanone to the dimer, 2-cyclopentylidenecyclopentanone (**9**), was selected for most intensive study with use of a refluxing solvent protocol. The in situ NMR studies suggested that zeolite HX would give reasonable activity without excessive trimer formation or secondary reactions at low temperature; this was borne out in the synthetic preparations. When the weight of zeolite was comparable to the weight of starting materials (e.g., 10 g of cyclopentanone and 8 g of HX in 100 mL of toluene), only a 50% theoretical yield of aldol products was

recovered. Much better results were achieved by reducing the amount of zeolite catalyst. For example, when 10 g of cyclopentanone, 2.5 g of HX, and 20 g of 3A molecular sieve were refluxed in 100 mL of toluene for 70 h, the yield of aldol products was 80%, and the selectivity for **9** was ca. 90% as determined by GC and quantitative solution state ^{13}C NMR. The remainder was mostly **10**.

Discussion

Reactivity. The order of activity of the various zeolites HZSM-5 > HY > HX > NaX, CsX > CsY, CsZSM-5 closely parallels our measurement of acidity using the method proposed by Farcasiu and co-workers based on the ^{13}C shifts of mesityl oxide. This suggests that the extent of proton transfer from the zeolite Bronsted sites to the ketones in the adsorption complex is important in establishing the probability that it will condense with a second ketone molecule.
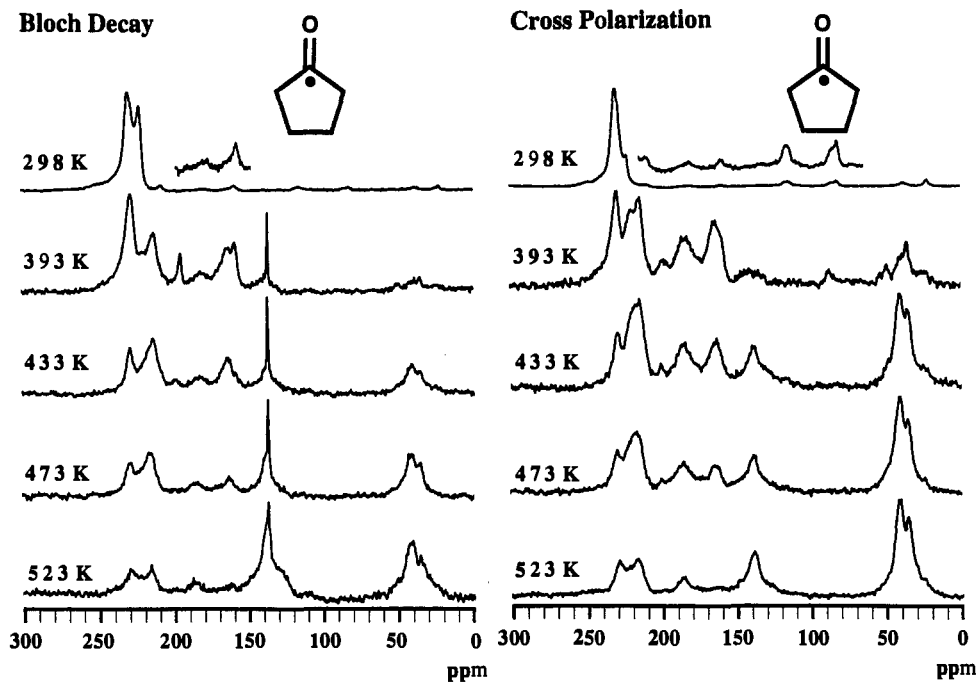
Bloch Decay   **Cross Polarization**

Figure 7. In situ 50.1-MHz ^{13}C MAS NMR study of the reactions of cyclopentanone-1-^{13}C on zeolite HX. Cyclopentanone was partially converted to trindane (138 ppm) at 393 K. Secondary reactions at higher temperatures, such as double bond migration, hydrogen transfer, and cracking, resulted in the resonances at 20–45 ppm.
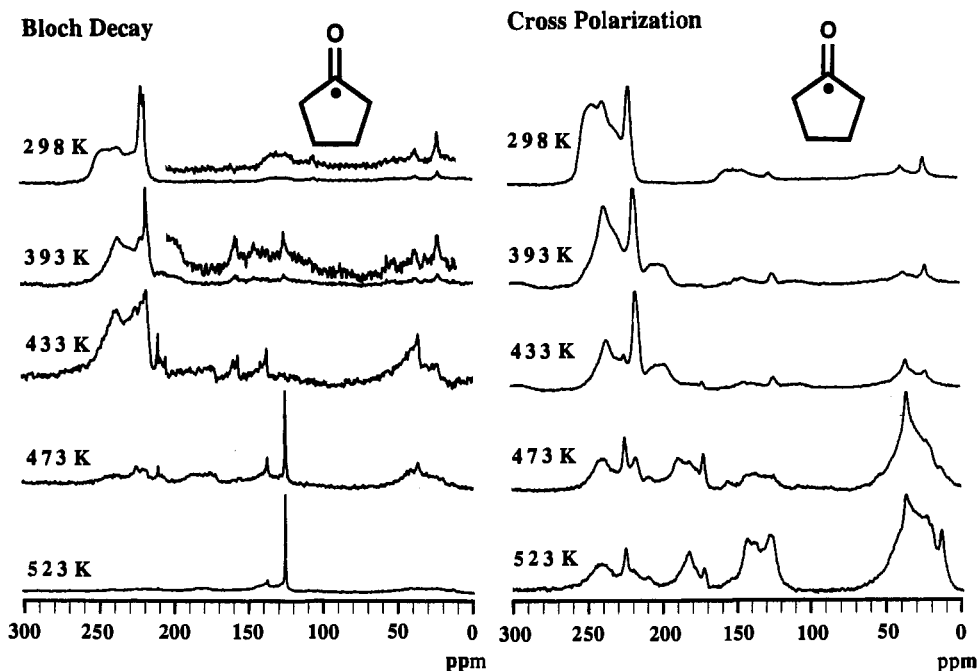
Bloch Decay   **Cross Polarization**

Figure 8. In situ 50.1-MHz ^{13}C MAS NMR study of the reactions of cyclopentanone-1-^{13}C on zeolite HZSM-5. No trindane formed in this medium-pore zeolite. The resonances in the 170–185-ppm region (CP spectra) indicated the formation of carboxylic acids, which decarboxylated to form CO_2 (126 ppm, Bloch decay spectra).

Zeolite CsX is classified as a weakly basic catalyst as a result of its activity for converting 2-propanol to acetone rather than propene[50,51] as well as its selectivity for side chain alkylation of toluene[52-55] rather than the ring alkylation observed with more acidic zeolites like HZSM-5. Consistent with this view, it is also believed that the activity of CsX for aldol chemistry also reflects

base catalysis.[56] But that is not clear from this study, in which the ketones did not have highly acidic methylene groups. It is impossible to fully exchange all of the Bronsted sites in X zeolite for Cs, and the catalyst we used had about 28% residual protons based on the difference from the analysis for Cs, Na, and Al. The NaX catalyst used also contained some residual Bronsted sites. If the aldol chemistry observed with these materials were base catalyzed, CsX should have been much more active than NaX; instead, the activity was comparable. If the Lewis acidity of the

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(51) Yashima, T.; Suzuki, H.; Hara, N. *J. Catal.* **1974**, *33*, 468–492.
(52) Hathaway, P. E.; Davis, M. E. *J. Catal.* **1989**, *119*, 497–507.
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(54) Engelhardt, J.; Szanyi, J.; Valyon, J. *J. Catal.* **1987**, *107*, 296–306.
(55) Mielczarski, E.; Davis, M. E. *Ind. Eng. Chem. Res.* **1990**, *29*, 1579–1582.

(56) Corma, A.; Fornés, V.; Martín-Aranda, R. M.; Garcia, H.; Primo, J. *Appl. Catal.* **1990**, *59*, 237–248.

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cations were important, NaX might have been more active than CsX. The fact that HX was more active than either CsX or NaX and that the more fully exchanged CsZSM-5 was almost completely inactive suggests that acid catalysis by the weak residual Bronsted sites rather than base catalysis may account for the results of this investigation. Recently it has been recognized that metal-exchanged X zeolites are properly viewed as bifunctional,[57] and it would not be surprising to find that even the very weak residual Bronsted sites are active in some transformations. The acidity of all of the zeolites was also manifested in the ready dehydration of the β-hydroxy ketones initially formed by aldol condensations.

The acidity of zeolite HZSM-5 is sufficiently strong that secondary reactions are important even at modest temperatures. This catalyst is useful for gas phase syntheses with short contact times or when the shape selectivity of medium pore zeolites is required for selectivity, but it may be necessary to learn to reduce the effective acidity using coadsorbates for some synthetic transformations.[6] In this study, the shape selectivity of HZSM-5 was manifested by the fact that only a trace of trindane formed from cyclopentanone on this catalyst, whereas that was an important product on the large-pore zeolite HX. Indeed, neither trindane nor its precursor **11** formed on CsX. The difference in selectivity with CsX vs HX can be rationalized in terms of the steric effect of a very large cation vs a very small cation.

Reaction Mechanism. None of the zeolites displayed superacidity at room temperature. No ¹³C signals characteristic of carbenium ions or hydroxycarbenium ions were seen in this study, and we doubt that such species are formed as long lived intermediates from ketones at the low reaction temperatures used in this study. The starting ketones, as well as products such as mesityl oxide, form adsorption complexes with partial proton transfer from the acid sites. On HZSM-5 the extent of proton transfer to mesityl oxide produces changes in ¹³C isotropic chemical shifts nearly identical with that observed by Farcasiu and co-workers in 70% sulfuric acid solution at room temperature.[38] This statement should not be construed to suggest that HZSM-5 is the same as 70% sulfuric acid but rather that the two media have very similar effects on the electronic structure of the mesityl oxide as mapped onto isotropic ¹³C shifts. This electronic change is implicated in the reactivity of the adsorbates. The other zeolites induce shifts in mesityl oxide that mimic correspondingly weaker acid solutions. On the basis of the results of this investigation, it is impossible to rule out free carbenium ions as transition states in the low-temperature aldol reactions, but it is appealing to consider the possibility that the reaction proceeds directly by bimolecular reaction between an adsorption complex and a free ketone.

The overall reaction sequences in Schemes 1 and 2 are similar to the aldol chemistry observed in other media. Dehydration of the intermediate β-hydroxyl ketones occurred readily in the zeolites. Trindane formed only in the large-pore zeolite HX. The unsymmetrical trimer **11** was not conclusively identified on any of the samples, but its formation is implicated as an intermediate in the synthesis of **12**. Species **10** can easily fit into the pore system of X and Y zeolites, but **11** is more sterically demanding, and the substitution of Cs⁺ for H⁺ deters its formation. Cracking and the other secondary reactions were reminiscent of flow reactor studies at higher temperatures and short contact times. The specific nature of these reactions can vary a great deal depending on the carbon skeleton of the ketone.[58]

¹³C-label retention occurred throughout, exactly as expected for both the aldol chemistry and the secondary reactions.

Synthesis. A number of studies prior to this one have made the case for the use of zeolites in organic synthesis. The present
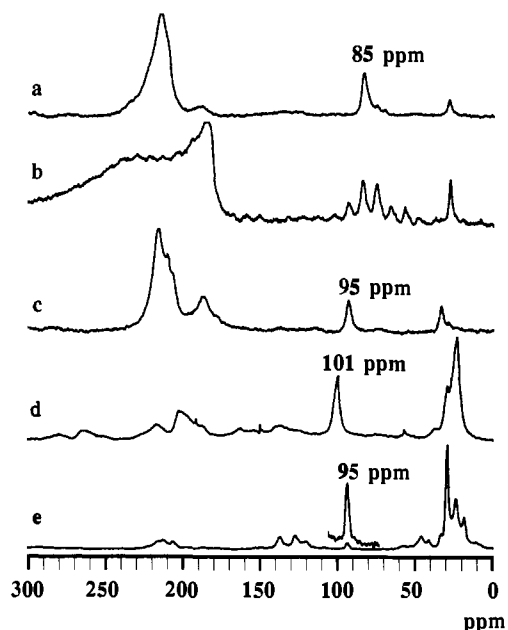
(57) Barthomeuf, D. *J. Phys. Chem.* **1984**, *88*, 42–45.
(58) Nováková, J.; Kubelková, L.; Jiru, P.; Beran, S.; Nedomová, K. In *Proceedings of the International Symposium on Zeolite Catalysis*; Acta Physica and Chemica Szegediensis: Szeged, 1985, pp 561–570.

Figure 9. Selected ¹³C spectra showing some features of the 85- and 95-ppm resonances on HZSM-5: (a) 50.1-MHz CP spectrum of acetone-2-¹³C at 298 K, showing the 85-ppm resonance; (b) 90.5-MHz CP spectrum of acetone-2-¹³C at 298 K with a spinning speed of 980 Hz, showing the spinning sidebands of the 85-ppm resonance; (c) 50.1-MHz Bloch decay spectrum of acetone-2-¹³C at 393 K showing the 95-ppm resonance; (d) 50.1-MHz CP spectrum of 2,4-pentanedione at 298 K; (e) 50.1-MHz CP spectrum of diacetone alcohol acquired at 298 K after heating at 393 K for 0.5 h. See the text for a complete explanation.

study has considered the reactivity trends observed with a series of zeolites with different acidities and/or pore sizes. The in situ ¹³C NMR protocol appears to be useful as a guide to the design of synthetic preparations as well as a mechanistic probe for articulating a systematic physical organic chemistry of zeolitic reaction media.

Spectral Curiosities of the Acetone/HZSM-5 System. As mentioned in the Results section, this system showed two odd signals, derived from the carbonyl carbon of acetone, that did not have any obvious chemical consequences. These species could not be isolated by extraction from the zeolite. These signals are easy to reproduce, and one of them has already been commented upon in the literature.[59] This section ends with a discussion of these features and some proposed assignments. This is primarily an exercise in spectral interpretation, but a better understanding of some of the more unusual species formed in zeolites may ultimately be of use in the development of a predictive chemistry. spectra from various ¹³C MAS studies are reported in Figure 9a–e. Spectra a and b in Figure 9 pertain to the resonance at 85 ppm. This species forms very early in the reaction of acetone-2-¹³C samples prepared at reduced temperatures, and it disappears simultaneously with the formation of mesityl oxide near room temperature. On the weakly acidic zeolites (e.g., CsX) a clear peak for diacetone alcohol (**2**) is seen at the expected value of 70 ppm early in the reaction of acetone-2-¹³C. In several studies of *tert*-butyl alcohol on HZSM-5, the alcohol reacted with an acid site and formed a new resonance that was variously reported as 77,[60] 81,[48] or 86 ppm.[61] This signal was assigned to the framework-bound alkoxy species **18**. Figure 9b shows that this 85-ppm peak displays a number of spinning sidebands at slow spinning speeds.

(59) Bosáček, V.; Kubelková, L.; Nováková, J. In *Catalysis and Adsorption by Zeolites*; Ohlmann, G., Pfeifer, H., Fricke, R. Eds.; Elsevier: Amsterdam, 1991; pp 337–346.
(60) Aronson, M. T.; Gorte, R. J.; Farneth, W. E.; White, D. *J. Am. Chem. Soc.* **1989**, *111*, 840–846.
(61) Stepanov, A. G.; Zamaraev, K. I.; Thomas, J. M. *Catal. Lett.* **1992**, *13*, 407–422.

This suggests a framework-bound species, possibly the analog of 18 formed from diacetone alcohol.

$$\begin{array}{c} CH_3 \\ | \\ H_3C-C-CH_3 \\ | \\ O \\ Si \diagup \quad \diagdown Al \end{array}$$
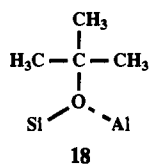
18

Figure 9c shows a representative spectrum from one of many studies in which a 95-ppm resonance formed in the vicinity of 393 K and persisted to ca. 433 K. This resonance formed in every study of acetone-2-^{13}C, regardless of whether additional water was coadsorbed. This species (reported at 93.7 ppm) was also seen in one[59] of the two[59,62] previously published ^{13}C NMR studies of acetone on HZSM-5. In ref 59, a natural abundance sample of acetone was spiked with a small amount of acetone-2-^{13}C. Signals were observed for all positions in that study. The 93.7-ppm signal was assigned to C-3 of 2,4-pentanedione, which has a ^{13}C chemical shift of 101 ppm in CDCl$_3$ solution at 298 K,[40] due to the keto–enol tautomerism. This assignment was a reasonable and attractive proposal. Unfortunately, all the reaction mechanisms which we can imagine for making 2,4-pentanedione result in C-3 derived from a methyl group on acetone, and the 95-ppm peak is never seen in our in situ studies of acetone-1,3-$^{13}C_2$. Figure 9d shows a spectrum of a high loading of natural abundance 2,4-pentanedione on HZSM-5 at room temperature; the ^{13}C chemical shift of C-3 is at 101 ppm, and there is no signal near 95 ppm.

We performed a large number of experiments in order to come up with a more satisfactory assignment for this resonance. The 95-ppm peak also formed from natural abundance diacetone alcohol (Figure 9e), but not from anhydrous mesityl oxide. It

always formed at a stage of the conversion of acetone corresponding to a high concentration of mesityl oxide. We are unable to prove a particular assignment for the 95-ppm resonance, but the most probable structure would be a hydrated ketone in equilibrium with mesityl oxide in the sterically demanding and acidic environment of HZSM-5.

Concluding Remarks

These studies have revealed many details of the reactions of simple ketones on zeolites of varying acidity and pore size. The chemistry can be conveniently divided into acid catalyzed aldol reactions and secondary reactions, such as double bond migration, hydrogen transfer, and cracking. Shape selectivity was clearly seen in the formation of trindane (**12**) from cyclopentanone on zeolites with the larger pores, but not on those with the smaller pores.

The starting ketones, as well as their various α,β-unsaturated products, formed reactive complexes with the Bronsted acid sites, resulting in ^{13}C chemical shift changes that clearly varied with the acidity of the zeolite as well as its activity for aldol chemistry. The ability to measure the effective acidity of the zeolitic environment under actual reaction conditions and relate it to reactivity suggests that a physical organic pedagogy for reactions in zeolitic media is emergent. The magnitude of the observed shifts demonstrates that the standard Bronsted sites of zeolites are not superacidic at low temperature.

In situ NMR studies of reactions on zeolites are useful not only for studies of reaction mechanisms but also as a guide to the design of synthetic preparations using zeolitic catalysts.

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