

A ^{13}C Solid-State NMR Study of the Chemisorption and Decomposition of Ethanol on MgO

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The adsorption and decomposition of ethanol on MgO have been studied by ^{13}C solid-state NMR, using the cross-polarization magic angle spinning technique (CP/MAS). The only chemisorbed species produced at room temperature is ethoxide. This is stable up to 200°C, above which temperature a complicated series of reactions sets in. The initial reaction leads to a surface *n*-butoxide species. At progressively higher temperatures the chemisorbed species include other alkoxides, together with acetate, carbonate, and hydrocarbon species. At the higher temperatures, various small molecules are observed in the gaseous and/or physisorbed state. These can be identified by conventional high-resolution NMR excited by 90° pulses. Experiments using ethanol enriched in ^{13}C at either C-1 or at C-2 show that no exchange occurs between these positions at temperatures up to 500°C. © 1986 Academic Press, Inc.

INTRODUCTION

The adsorption and reaction of ethanol on MgO have previously been studied by various workers (1-6). These studies have generally involved infrared spectroscopy of the adsorbed phase, or analysis of the gas phase under steady-state reaction conditions. Species identified by these techniques have typically included surface ethoxide and acetate, together with gaseous H_2 , acetaldehyde, and butadiene.

Since high-resolution NMR may identify species which do not appear prominent in the infrared because of low extinction coefficients, we thought it of interest to reinvestigate this system using NMR techniques. This work continues previous NMR studies of methanol on MgO from this laboratory (7, 8).

EXPERIMENTAL

The NMR apparatus used has previously been described (7). Magic angle spinning of sealed samples was performed using the spinner described in (9). Solid-state NMR spectra were obtained using single-contact Hartmann-Hahn cross polarizations. Normally a spin-locking and decoupling field

strength of 55 kHz was used, with a 2 ms contact time. Samples were spun at the magic angle at 1.8 to 2.4 kHz. In the low field (1.4 T) used for these experiments, no spinning sidebands are visible at these speeds. The magic angle was correctly set within $\pm 0.1^\circ$, leading to a typical linewidth of 6 to 8 Hz for sp^2 carbons in well-crystallized solids. Spectra were also obtained by excitation of ^{13}C with 90° pulses, while continuously decoupling protons with a field of 20 kHz.

Magnesium oxide was prepared from $\text{Mg}(\text{OH})_2$ as previously described (8). It had a specific surface area of 220 $\text{m}^2 \text{g}^{-1}$ and a bulk density of 0.6 g cm^{-3} . Ethanol was doubly distilled over Mg metal, and stored over predried molecular sieves. Ethanol enriched to 90% ^{13}C at either the 1- or 2-position was prepared by reduction of the corresponding acetate (10). The enriched sodium acetate samples were from MSD Isotopes Ltd. Doubly enriched acetaldehyde was also obtained from MSD Isotopes.

Samples were prepared from MgO which was vacuum degassed 16 h at 500°C. Ethanol vapor was allowed to adsorb from the gas phase after the MgO had been cooled to

room temperature. The amount of ethanol adsorbed was measured by conventional gas-volumetric techniques. After adsorption, samples were cooled to 77 K to prevent pyrolysis of residual ethanol vapor, and sealed off. The sealed samples were kept at room temperature for several hours before NMR measurements. Repetition of NMR measurements showed that the samples did not change on a timescale of days at room temperature.

After recording of initial spectra, the samples were heated to various temperatures for known lengths of time and then recooled to room temperature, and the NMR spectrum was redetermined. All NMR measurements were made at room temperature. During this heating process some unknown fraction of the adsorbed ethanol would be expected to desorb. This aspect of the experiments was not closely

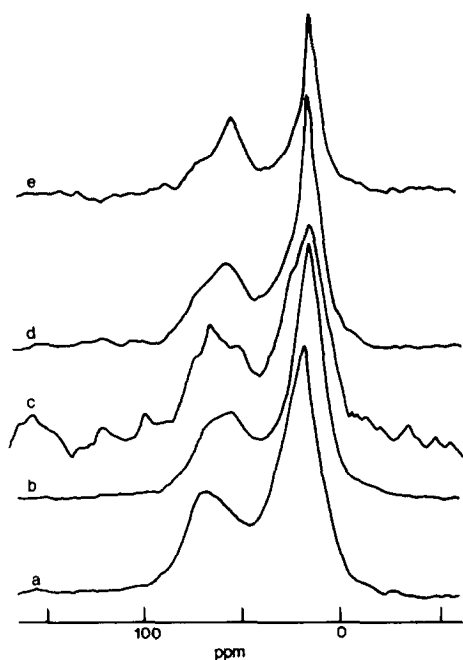


FIG. 1. ^{13}C cross-polarization spectra of static samples of natural ethanol on MgO, for various coverages. (a) $4.19 \mu\text{mole}/\text{m}^2$, 3.2×10^5 contacts, (b) $5.42 \mu\text{mole}/\text{m}^2$, 4.7×10^5 contacts, (c) $6.11 \mu\text{mole}/\text{m}^2$, 1.1×10^6 contacts, (d) $7.19 \mu\text{mole}/\text{m}^2$, 4.7×10^6 contacts, (e) $8.92 \mu\text{mole}/\text{m}^2$, 6.6×10^6 contacts. Spectra are not normalized for varying numbers of scans.

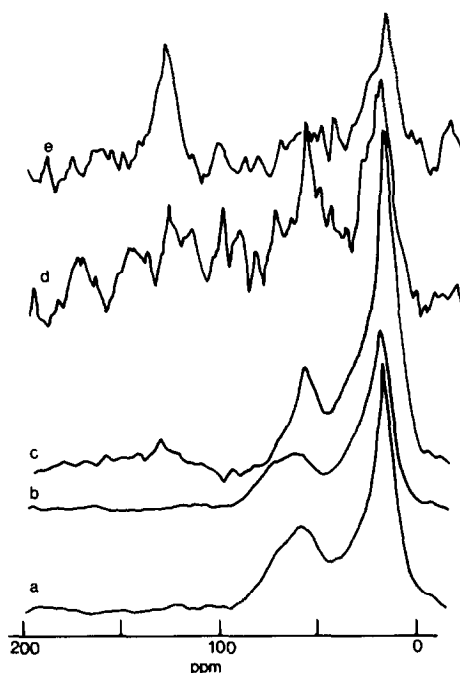


FIG. 2. Spectra of sample from Fig. 1d, after heating for 3 h at various temperatures. (a) Room temperature, (b) 180°C , (c) 350°C , (d) 500°C , (e) same as (d), but spectrum excited by 90° pulses, instead of cross-polarization.

controlled. The sample tube sizes and amounts of adsorbed ethanol were such that the pressure of gaseous ethanol would always be less than 1 atm, even assuming complete desorption.

RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C spectra of ethanol on MgO at various coverages, recorded on a static sample. As can be seen, a broad powder pattern is found, which is rather similar to that which we obtain with a sample of $\text{Mg}(\text{OC}_2\text{H}_5)_2$. The broadness arises mainly from the chemical shift anisotropy of the carbon atoms, that of the CH_2 group being, as usual (11), greater than that of the CH_3 .

Figure 2 shows the thermal evolution observed on static samples after heating to progressively higher temperatures. Clearly reaction has taken place, but because of the broadness of the lines, it is difficult to identify the products.

Once magic angle spinning is employed, the situation changes dramatically. Narrow lines are now obtained, because of the suppression of chemical shift anisotropy. Figures 3 to 6 show spectra for samples heated to various temperatures. Spectra obtained by cross-polarization are shown in Figs. 3 and 4, and spectra obtained by 90° pulses with ^1H decoupling in Figs. 5 and 6.

Since cross-polarization depends on the proton-carbon dipolar coupling, spectra obtained by this technique discriminate in favor of static carbons which are close to a proton. There will be little signal from rapidly moving physisorbed or gaseous species where the dipolar interaction is motionally

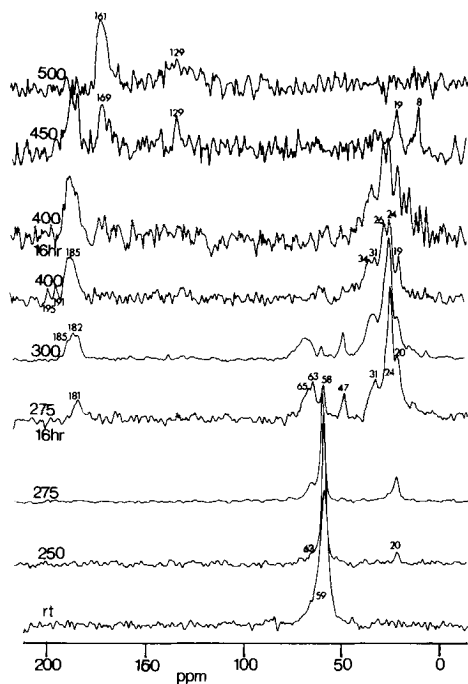


FIG. 3. CP/MAS spectra of ethanol, 90% $1\text{-}^{13}\text{C}$ on MgO, at a coverage of $1.3 \mu\text{mole}/\text{m}^2$. Samples heated at the indicated temperature for 3 h, except as noted. Spectra recorded with 10^3 to 2×10^4 scans. Spectra have been normalized before plotting to compensate for varying numbers of scans. In this and subsequent figures, species may be qualitatively identified from their resonance position (in ppm) as follows: -10: CH_4 , 5: C_2H_6 , 10-25: $-\text{CH}_3$, 20-35: $-\text{CH}_2-$, 30-50: highly branched aliphatics, 49: $-\text{OCH}_3$, 55-70: other alkoxides, 110-150: alkenes and aromatics, 160-170: CO_3^{2-} and HCO_3^- , 170-185: RCOOR' .

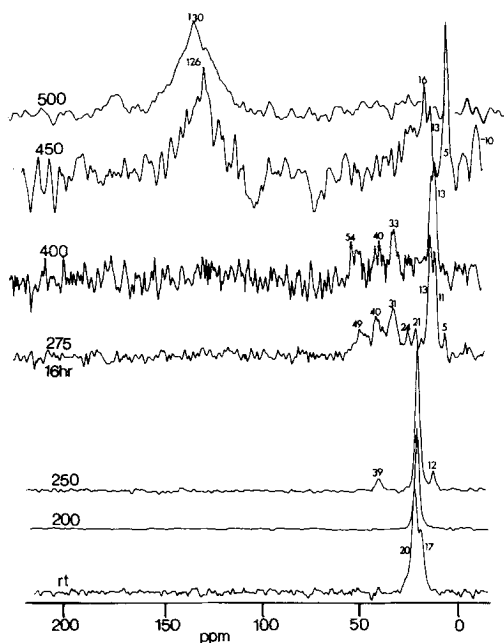


FIG. 4. CP/MAS spectra as in Fig. 3, but ethanol is 90% $2\text{-}^{13}\text{C}$.

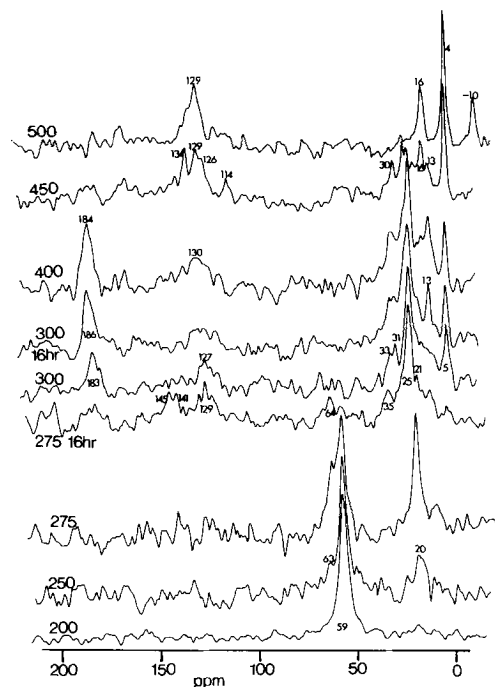


FIG. 5. MAS spectra excited by 90° pulses. 90% $1\text{-}^{13}\text{C}$ ethanol on MgO.

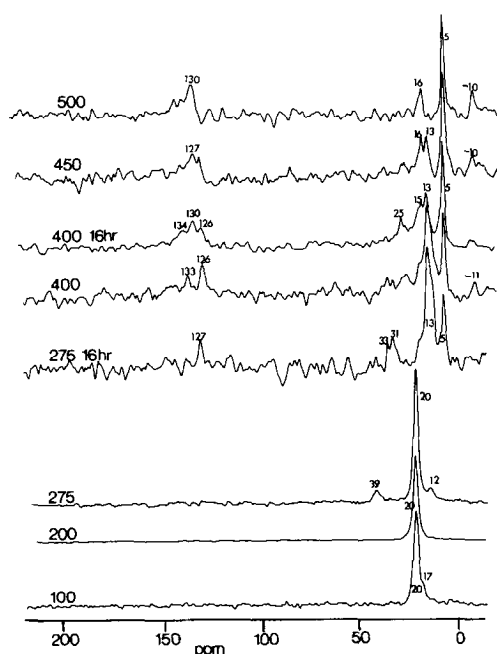


FIG. 6. MAS spectra excited by 90° pulses. 90% ^{13}C ethanol on MgO .

averaged. The 90° pulse spectra in principle detect all carbons in the sample. However, we have used a repetition rate of 1 Hz, which will discriminate against species of long ^{13}C spin-lattice relaxation time. These would be expected to be primarily rigidly bound surface species. Due to continuous proton decoupling, mobile carbons bound to protons will be further enhanced by the nuclear Overhauser effect. Thus to a good approximation, species seen with cross-polarization and not with 90° pulses are strongly bound surface species, whereas those seen only with 90° pulses are mobile species. It is of course possible for a species to be detected with both types of excitation, particularly if it is bound to the surface and undergoing fairly rapid anisotropic motion, which will relax ^{13}C without completely averaging out the dipolar coupling. An example of this is the surface ethoxide species seen in all spectra before heat treatment.

Figures 3 and 5 show spectra obtained with ethanol 90% enriched at the CH_2 posi-

tion, whereas Figs. 4 and 6 are for enrichment at the CH_3 group. The 1% of natural ^{13}C at the unenriched positions makes a negligible contribution to the spectra under our conditions. Thus these spectra permit a determination of the state and thermal evolution of each carbon separately.

The spectra taken before any heat treatment show a CH_2 line at 59 ppm and CH_3 lines at 17 and 20 ppm. For comparison, the shifts of liquid ethanol are 57.3 and 17.9 ppm (12) whereas we measure 58.8 and 22.5 ppm for solid $\text{Mg}(\text{OCH}_2\text{CH}_3)_2$. Since the lines of this initial species are broadened by chemical shift anisotropy in the static spectra, it is clearly an ethoxide species bound to the surface. It is interesting that the methyl peak is split into two components. This is possibly due to ethoxides in different environments on the surface; methyl shifts are known to be sensitive to steric effects (12). It is unlikely that the line at 17 ppm arises from a physically adsorbed ethanol, since it is relatively smaller in the spectrum obtained with 90° pulses than in the cross-polarization spectrum. On heating to 200°C , the methyl lines coalesce into a single line at 20 ppm, and the methylene line narrows considerably. This is similar to the behavior observed for methanol on MgO (8). It probably represents the thermal annealing of the adsorbed layer into a more regular array of adspecies than is produced by random adsorption at room temperature.

The first reaction products appear after heating to 250°C . The initial reaction leads to peaks at 63 and 20 ppm arising from the CH_2 group of the ethanol, and at 39 and 12 ppm from the CH_3 group. Since we always find that these species appear in parallel, it seems that the initial reaction produces a four-carbon species on the surface. The question then arises as to what this four-carbon species is. Clearly it contains a methyl group (12 ppm) and a C-O bond (63 ppm). If we continue to make the tacit assumption, which works for methanol, ethanol, and isopropanol (13) that surface alk-

oxide species have shifts near the corresponding values for the liquid alcohols, there does not seem to be any single species which will account for all four peaks. However, this assumption may be wrong; experimentation soon shows that it is.

Figure 7 shows the cross-polarization spectra for *n*-butanol of natural isotopic abundance on MgO at two coverages. We observe peaks at 13, 20, and 64 ppm, together with a composite peak at about 40 ppm. This appears to contain two components with shifts of about 36 and 41 ppm whose relative proportions vary as the coverage is changed. It is clear that the product peaks formed from ethanol are consistent with what we observe for *adsorbed n*-butanol, and we therefore assign the initial ethanol reaction product as a surface *n*-butoxide species.

This leaves an interesting question. Why the large difference in C-2 shift between liquid *n*-butanol (35.3 ppm (12)) and surface butoxide? This difference of as much as 6 ppm is more than we have observed for any of the smaller alcohols. It also occurs at C-2, whereas C-1 should be the carbon most strongly interacting with the surface. We

believe that this is probably a conformational effect. Conformational effects on ^{13}C shifts are known to be quite large (12). In liquids at room temperature conformational interchange is normally so rapid that only an average shift is observed. In suitable systems, low temperature experiments permit separate lines of the individual conformers to be seen. For a long molecule firmly attached to a surface at one end, it is likely that conformational interchanges will be relatively restricted, and the range of possible conformers different from that available in the liquid. We believe this is a reasonable explanation for the line splitting and large shift of C-2 in adsorbed *n*-butoxide, and the nonoccurrence of such effects with smaller surface alkoxides.

It is interesting to note that a similar splitting of the C-2 resonance has been observed by Dawson *et al.* (14) for *n*-butylamine on Al_2O_3 . The explanation may be similar, although the situation is complicated by the probable existence of differing types of acid sites on the Al_2O_3 surface.

The isotopic labeling results in Figs. 3 and 4 make clear the source of the various carbons in the *n*-butoxide product. Thus it can be seen that C-1 and C-3 arise from the ethanol CH_2 carbon, whereas C-2 and C-4 arise from CH_3 . This information places constraints on possible reaction mechanisms.

An obvious mechanistic suggestion is that dehydrogenation of ethanol leads to acetaldehyde, which then undergoes an aldol condensation. The subsequent transformations of aldol to crotonaldehyde, *n*-butyraldehyde, and *n*-butanol seem plausible, if both dehydrogenation and dehydration equilibria are established on the surface of the catalyst. This suggestion can be tested, to some extent, by adsorbing acetaldehyde on the catalyst. Figure 8 shows the spectrum obtained from unenriched acetaldehyde interacting with the catalyst at room temperature. The many product peaks indicate a complex series of reactions, and show that the initial reaction of ethanol is

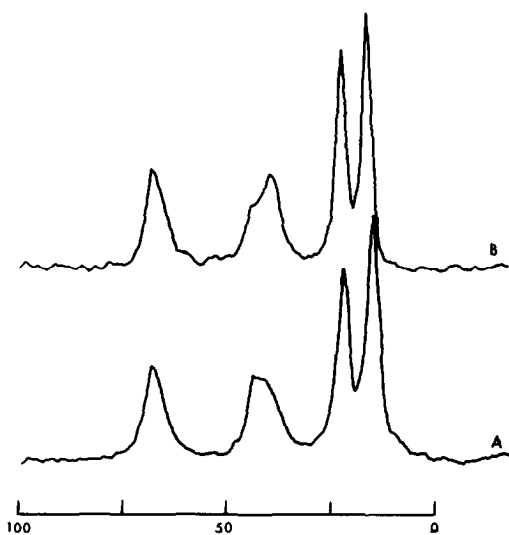


FIG. 7. CP/MAS spectrum of natural *n*-butanol on MgO. (A) $3.4 \mu\text{mole}/\text{m}^2$, 1.2×10^3 contacts, (B) $6.8 \mu\text{mole}/\text{m}^2$, 5.9×10^4 contacts.

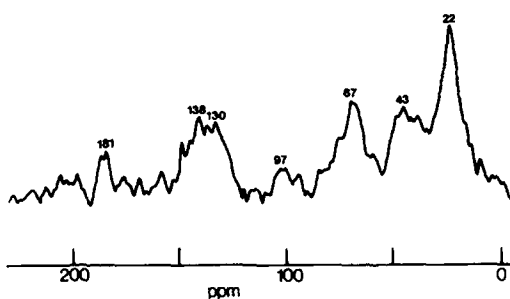


FIG. 8. CP/MAS spectrum of natural CH_3CHO on MgO . Coverage $13.9 \mu\text{mole/m}^2$, 1.7×10^5 contacts.

not a simple dehydrogenation followed by acetaldehyde chemistry.

This is not a conclusive demonstration, however, since it might be asserted that acetaldehyde chemistry is different on a surface largely covered with chemisorbed ethanol. We have therefore studied systems in which isotopically natural ethanol was first adsorbed on the catalyst, heated to 200°C to equilibrate the adsorbed layer, and then cooled to room temperature. Then a smaller amount (18% of adlayer) of doubly ^{13}C -labeled acetaldehyde was added. Figure 9 shows the results of such an experiment. As can be seen, the initial spectrum (Fig. 9A) reveals only peaks at 19 and 57 ppm.

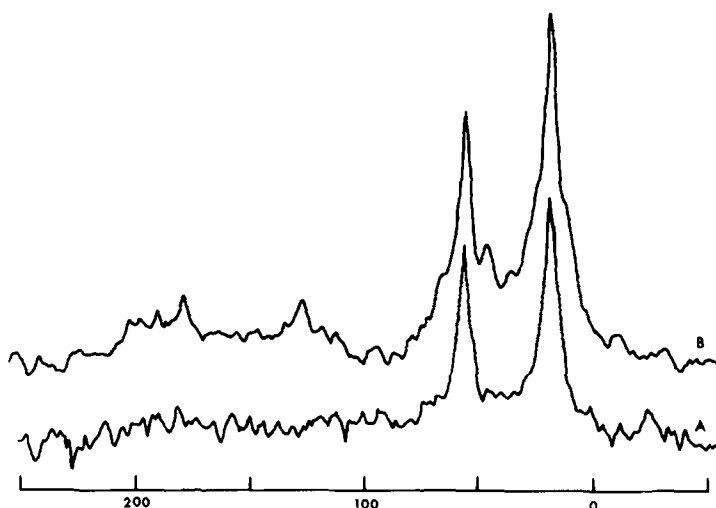


FIG. 9. CP/MAS spectrum of 90% doubly ^{13}C -enriched acetaldehyde, $0.31 \mu\text{mole/m}^2$ on MgO with $1.39 \mu\text{mole/m}^2$ preadsorbed natural ethanol. (A) Room temperature, 1.4×10^5 contacts, (B) Heated 1 h to 250°C , 1.3×10^5 contacts.

This is the spectrum of ethanol, not of acetaldehyde. Integration of these peaks shows that they comprise slightly over 50% of the ^{13}C in the sample. The remainder is presumably in the very broad peak lying between 100 and 200 ppm, which cannot be integrated with accuracy. Thus the room temperature reactions of acetaldehyde in the presence of excess ethanol appear to comprise isotopic exchange with the ethanol, together with polymerization.

Heating the mixed sample to 250°C produces substantial reaction (Fig. 9B). However, this is of a much more complex nature than is observed on heating an adsorbed ethanol layer to the same or higher temperature. Thus we conclude that the dehydrogenation–hydrogenation equilibrium of ethanol is probably established in times of the order of 1 day at room temperature, accounting for the isotopic exchange between ethanol and acetaldehyde. However, the acetaldehyde formed in this reaction does not appear to be an important part of the subsequent high temperature reaction of ethanol on MgO .

From Figs. 3 and 4 we see that the next stage of the thermal reaction occurs at 275 – 300°C . The *n*-butoxide peaks have grown,

and new reaction products are visible. The ethanol CH₂ group has given rise to peaks at 180–185 ppm (carboxylate), 65 ppm (alkoxide), 47 ppm (methoxide ?), 31 and 24 ppm (CH_n). A peak at 31 ppm is typical of CH₂ in the interior of a long alkyl chain, and at 24 ppm of CH₂ adjacent to CH₃. In view of the possibility of conformational effects, as discussed above for the *n*-butoxide group, it does not appear practical to define these species more closely.

The methyl carbon, meanwhile, has given rise to peaks at 31, 13, and 11 ppm and to smaller peaks at 49, 24, and 21 ppm. The peaks at 11 and 13 ppm are clearly aliphatic methyl groups. The most reasonable surface carboxylate in this system would be acetate, which is consistent with peaks at 24 and 180–185 ppm (15). The peak at 49 ppm probably arises from methoxide (8). The only reasonable alternative would be a highly branched hydrocarbon structure (16) which should give rise to other characteristic peaks.

Figures 5 and 6 show the appearance of a peak at 5 ppm (C₂H₆) arising from both carbons, together with small peaks in the range 126–145 ppm. The latter are probably small olefins, since they do not show up in the cross-polarization spectra. The presence of ethane shows the occurrence of a formal reduction, necessary to balance the formal oxidation leading to acetate. It should be noted that the ethane formation reaction must be essentially nonreversible under our conditions, since ethane arises from both ethanol carbons, but isotopic scrambling is never observed in the residual chemisorbed species. Probably ethane results from reduction of ethylene produced by dehydration.

Thus the intermediate stage of the reaction can be interpreted as a further chain growth in surface alkoxides, presumably by a repetition of the mechanism leading to the initial *n*-butoxide. Simultaneously surface acetate and methoxide appear, together with gaseous ethane.

As heating is continued to still higher tem-

peratures, we see first the disappearance of surface alkoxides at 400°C, and accompanying growth of the surface acetate. As the temperature is raised, peaks in the range 160–170 ppm appear from the ethanol CH₂ group. These are undoubtedly surface carbonate species (8). Simultaneously small peaks at 129, 19, and 8 ppm appear. The last is an unusual shift for a bound species. Such shifts most commonly occur for the CH₃ group of a C₂H₅ fragment which is bound to a quaternary carbon in a branched hydrocarbon (16) or tertiary alcohol (17) structure. Thus there is perhaps evidence for a small amount of branched chain formation.

At the highest temperatures studied, we find that the only significant surface species from the ethanol CH₂ group is the surface carbonate. The CH₃ group, on the other hand, has produced a broad peak centered at about 130 ppm. This probably results from overlapping resonances of condensed aromatic hydrocarbons. It is remarkable that the identity of the two ethanol carbons is preserved, and no scrambling has occurred even at 500°C.

At 450–500°C, the 90° pulse excited spectra show peaks at –10 ppm (methane) and 16 ppm (propane) arising from molecules which are gaseous or only physically adsorbed. These molecules involve carbon from both of the original ethanol sites. It is probable that the gas phase also contains substantial H₂ and CO not visible by NMR, as is the case for the methanol/MgO system (8).

SUMMARY

The present results, although not pertaining to very well-defined reaction conditions, illustrate the considerable power of CP/MAS spectroscopy for the elucidation of surface reaction mechanisms. It would not be difficult to imagine quenching a sample from a steady-state flow reaction system in a way suitable for such studies. This would be rather expensive if enriched reactants were used, but as Figs. 7 and 8 illus-

trate, the experiments are possible with natural abundance materials, at the cost of more spectrometer time and less mechanistic specificity.

We have not attempted to quantify the concentrations of surface species. For cross-polarization measurements this requires a knowledge of cross-polarization dynamics and of laboratory and rotating-frame relaxation times. A more detailed study of the methanol/MgO system (8) showed that these parameters are favorable in that case, and that good quantitative measurements could be made. This conclusion can probably be extrapolated to other surface alkoxide species. With the use of enriched samples, it is entirely feasible to make the necessary measurements in other cases to establish the degree of quantitative reliability.

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