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NMR Studies of Olefin Adsorption on Zinc Oxide

Nuclear magnetic resonance has been used for surface studies of molecular motion, (*1*), orientation (*2*) and chemical interactions (*3*). Because of the inherent insensitivity of NMR most of these studies have been restricted to systems of large surface area, and to coverages greater than a monolayer.

We report here 100 MHz proton resonance studies of several chemisorbed species at a surface area of less than 10 m^2/g with coverages of less than a monolayer.

The adsorption of the light olefins on zinc oxide has been the subject of extensive infrared and kinetic investigations by Connor *et al.* (*4*) Connor and Kokes (*5*) and Dent and Kokes (*6–11*) which provide excellent material for comparison.

The NMR spectra were recorded at 100 MHz utilizing a Varian XL-100 spectrometer, with 12 mm sample tubes, and external lock. The homogeneity of the magnet was trimmed by using a double sample tube with zinc oxide in the outside, and tetramethylsilane (TMS) or dimethyl sulfoxide (DMSO) in a concentric inner tube.

Gases used were Matheson C.P. grade. The zinc oxide was Kadox-25 from the New Jersey Zinc Company, and had a surface area of 9 m^2/g (BET). It was treated as in investigations (*4–11*); evacuated for 2 hr at 450°C, heated in 160 Torr of O_2 at 450° for a further 2 hr with a liquid nitrogen trap in the system, cooled to room temperature, then evacuated again for 1 hr.

Figures 1a and 1b show the NMR spectra of ethane and *n*-butane physically adsorbed on ZnO, which were recorded for purposes of comparison. Figure 2a shows the spectrum of ethylene at a coverage of 1.25×10^{-5} moles/g (approx 0.2 monolayers). Figure 2b shows the spectrum of propene at a coverage of 3.1×10^{-5} moles/g. All of these spectra were recorded at room temperature. The lines are broad, having a full width at half-height of 30 to 120 Hz, presumably due to partially averaged dipole–dipole interaction (line width is not changed by spinning). Spin–spin splitting is not resolved. As shown, however, the resolution is good enough to distinguish CH_3–, –CH_2–, and olefinic protons.

Chemical shifts of the adsorbed species were measured relative to external TMS samples. The values were corrected by —0.7 ppm for the difference in diamagnetic susceptibilities of ZnO and TMS, using the long cylinder aproximation (*12*). The volume susceptibility of ZnO was calculated using the observed bulk density of the powder, and the data of Trew *et al.* (*13*). These results are presented in Table 1, together with the chemical shifts observed by other workers (*14–16*) for the nonadsorbed molecules.

As shown, the physically adsorbed paraffins have no chemical shift relative to the free molecules, within our experimental uncertainty.

In contrast, the adsorbed olefin reso-

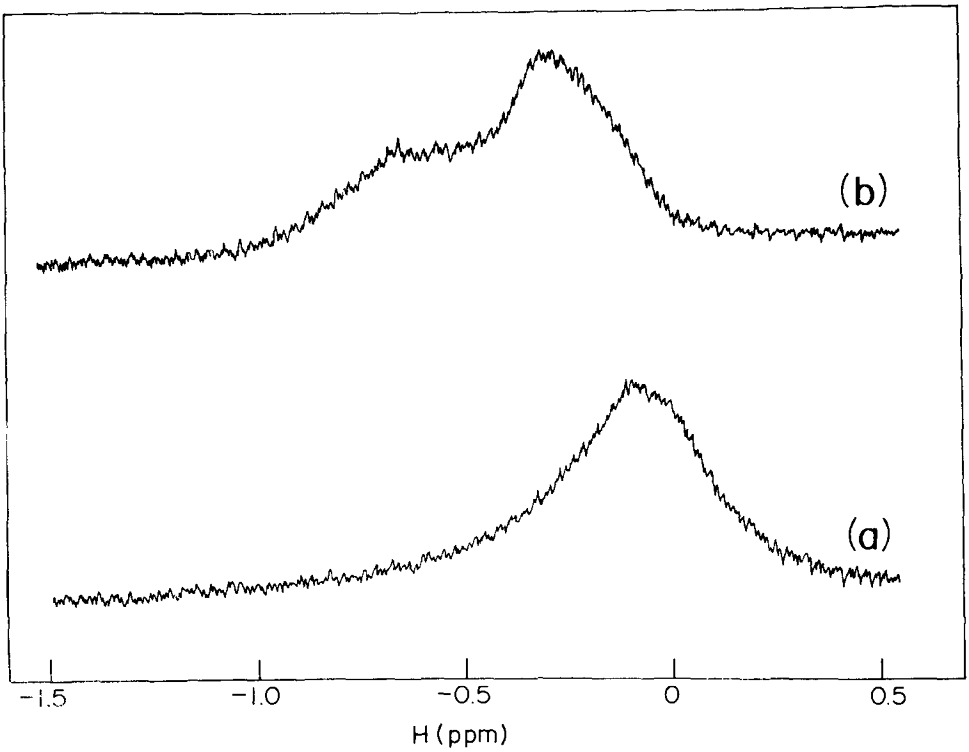
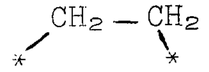


FIG. 1. 100 MHz NMR spectra of: (a) C_2H_6; and (b) n-C_4H_{10} physically adsorbed on ZnO. Magnetic field is in parts per million relative to external TMS, uncorrected.

nances are downfield from the corresponding free molecules by 0.6 to 0.8 ppm, except for the CH_3 protons of C_3H_6. It thus appears that the olefins undergo a specific chemical interaction, with deshielding of the protons, due to electron donation into the surface. This conclusion is substantiated by the line widths, which are broader for the olefins than for the paraffins (120 Hz full width at half maximum for C_2H_4 vs 36 Hz for C_2H_6), indicating more rigidly bound molecules.

Our results for ethylene are in excellent agreement with those of Dent and Kokes (*9*) who propose adsorption as a π-complex. Our results appear to exclude any such structures as



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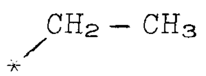

since the only resonance observed is in the olefinic region.

For propene, the situation is more complex. Dent and Kokes (*10*, *11*) find that C_3H_6 adsorption leads to both a strongly bound state, for which they propose a π-allyl structure, and a more weakly bound state, thought to be a π-complex, which can be desorbed by pumping at room temperature. We find, as do Dent and Kokes, that about half of the adsorbed propene can be desorbed at room temperature. We have so far been unable to obtain NMR spectra of the tightly adsorbed residue, probably because tight binding produces a line width too broad to observe on the present instrument. Further investigations with pulsed NMR techniques are under way. We conclude then, that our present propene spectra arise wholly from the weakly adsorbed population. Our results strongly support a π-complex structure for this species since: (a) no methylene resonance is found; and

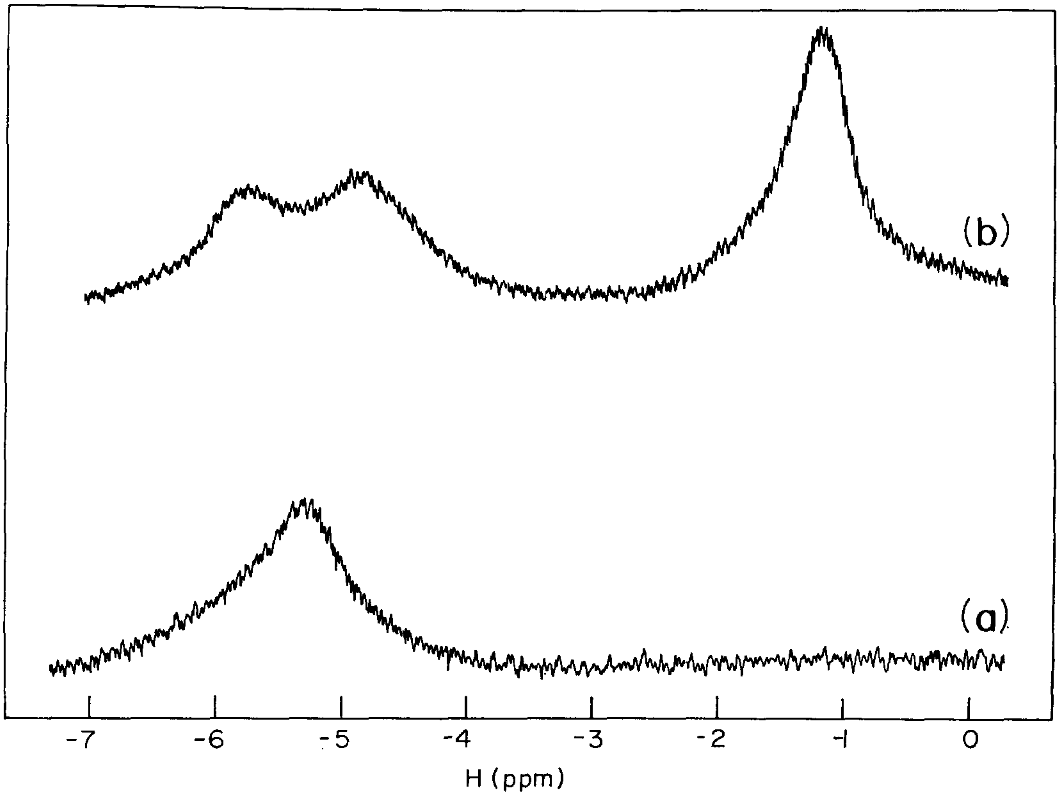

Fig. 2. 100 MHz NMR spectra of: (a) C_2H_4; and (b) C_3H_6 adsorbed on ZnO. Field units as in Fig. 1.

(b) the chemical shift displacement on adsorption is much greater for the olefinic protons than for the methyl protons. The observation of only two bands in the olefinic region is not surprising, since two of the free molecule chemical shifts are nearly the same in comparison with our observed line widths.

We have carried out some preliminary experiments on the interaction of the linear butenes with ZnO. In these experiments, it is possible to observe the spectrum of 1-butene changing in time to that of the 2-butenes as the catalytic isomerization takes place. We propose to report on these studies in more detail later.

TABLE 1

Chemical Shifts of Free and Adsorbed Molecules
(ppm from external TMS, corrected)

Molecule	δCH_3	δCH_2	δ olefinic
C_2H_6	−0.9 ppm	—	—
C_2H_6 (ads)	−0.8	—	—
n-C_4H_{10}	−0.9	−1.3	—
n-C_4H_{10} (ads)	−1.0	−1.4	—
C_2H_4	—	—	−5.3
C_2H_4 (ads)	—	—	−6.1
C_3H_6	−1.7	—	−4.9, −5.0, −5.7
C_3H_6 (ads)	−1.9	—	−5.5, −6.5

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The Shift of CH Stretching Band of Surface Alcoholate on Metal Oxides

The frequency of the various types of vibration in molecules is influenced by internal or external environments (*1, 2*). The infrared spectra of adsorbed species should, therefore, be closely related to the nature of the catalyst. Kiselev (*3*) showed recently that the absorption band originating in free hydroxyl groups on a silica surface shifted to lower frequencies when hydrogen bonding occurred with organic compounds, and the shift of the band increased with the increase of the heat of adsorption of these compounds. Cook (*4*) found that the frequency of —C=O stretching vibration in xanthone shifted due to the interaction with metal halides; the acidity of the halides was correlated with the shift.

In the present note, the authors show that the absorption bands due to CH asymmetric stretching vibration in a terminal methyl group is strongly influenced by the nature of metal oxides when surface normal alcoholates are formed on the oxides.

EXPERIMENTAL

Experiments were carried out in a manner similar to that in our previous work (*5*). Magnesium oxide sample (Kishida Chem. Co. Ltd., Guaranteed grade) was prepared by compacting the powder at a pressure of 210 kg/cm^2 in a steel die to form a self-supporting disc of about 50 mg/cm^2.

Before the run, the disc was degassed at 700°C for 30 min and then heated in oxygen under a pressure of 5 cm Hg for 1 hr