Chemical Reactions of Alkenes and Alkynes with Solid-State Defects on ZSM-5

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The identification of solid-state defects on calcined H-ZSM-5 powder is discussed in terms of positive holes on oxygen atoms between the tetrahedral structure of silica–alumina. Photoelectron studies of water molecules add new insight into the localized nature of the unpaired electron on the solid-state defects. A charge transfer mechanism between the unsaturated organic molecules and these defects is responsible for the subsequent chemical events. Intramolecular rearrangement of the 3,3-dimethyl-1-butene radical cation yields a more stable 2,3-dimethyl-2-butene isomer radical cation, whereas aromatization of the 2-butyne radical cation forms hexamethylbenzene radical cation at higher temperatures. On the basis of direct observations of these chemical reactions, both the solid-state defects and various pathways of radical cations should play an interesting role in understanding zeolite catalysis.

INTRODUCTION

For three decades, the discussion of the active sites on zeolites or other silica–alumina materials has been concentrated about the existence and involvement of either Brønsted acidic or Lewis acidic sites (*1, 2*). Both Weisz (*3*) and Rabo and Poutsma (*4*) have reviewed numerous technical papers for involvement of one or the other type of sites. They concluded that the catalytic loci are most likely centered on positions which are called "solid-state defects." These sites tend to elude characterization by ir spectroscopy, X-ray crystallography, and thermal analyses. However, the intrinsic unpaired electron in the proposed structure of solid-state defects they described, should be observable by electron spin resonance and photoelectron spectroscopy techniques. These two modern instruments would complement each other in understanding the molecule–solid interaction on a zeolitic surface and their chemical transformation inside the three-dimensional channels of the zeolites.

The present work was undertaken to obtain information on solid-state defects, organic cation radical formation, and the radical cation's chemical rearrangement under various experimental conditions.

EXPERIMENTAL METHODS

H-ZSM-5 was prepared by the procedures described in the literature (*5*). After ignition, the chemical analysis was: Na_2O, 1.50%; Al_2O_3, 3.6%; SiO_2, 95.0%. Sodium ions were further exchanged by ammonium ions. After drying the solid samples in the oven at 150°C overnight, the solid catalysts were pretreated with oxygen for 1 h at 500°C and evacuated at the same temperature for another 2 h. After the samples cooled to room temperature, the catalyst was transferred under vacuum to standard ESR sample tubes and sealed. Both alkene and alkyne vapors were deposited on the catalyst at low temperature by use of a vacuum line. The electron spin resonance spectra were recorded on a Varian 4505 spectrometer with 100-kHz modulation and a dual cavity. Measurements were carried out in the range 77 to 477 K and g values were determined by comparison with DPPH and a Varian weak pitch sample.
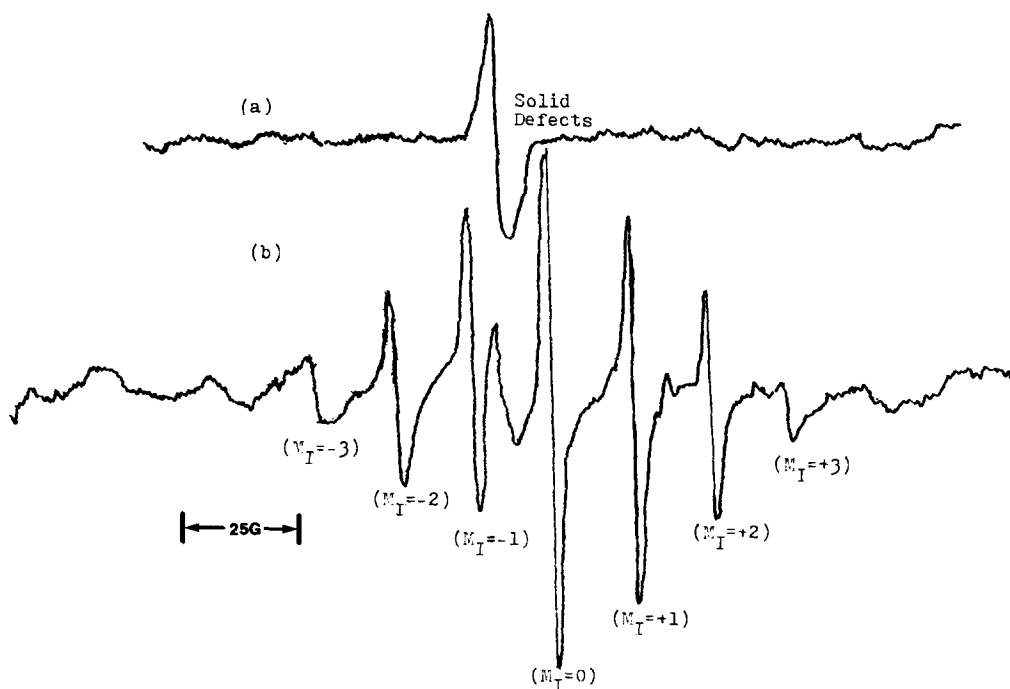
FIG. 1. (a) ESR spectrum for solid defects on the ZSM-5 surface at 123 K. (b) ESR spectrum of 3,3-dimethyl-1-butene chemisorbed on the ZSM-5 surface at 123 K.

EXPERIMENTAL RESULTS

The electron spin resonance spectrum of the solid-state defects on the ZSM-5 at 123 K is shown in Fig. 1a. During the adsorption of 3,3-dimethyl-1-butene, the ESR signal of solid-state defects decreased and a new set of isotropic ESR lines with center $g = 2.0028 \pm 0.0002$ developed at room temperature. The proton hyperfine splitting was measured: $a_H = 17.5$ G which is not expected for the 3,3-dimethyl-1-butene radical cation. Because of intramolecular rearrangement, it is assigned to the ESR spectrum of the 2,3-dimethyl-2-butene radical cation (Fig. 2). Further temperature-dependence studies did not change the proton hyperfine splittings of the four methyl groups significantly.

The 2-butyne molecule is a linear polyatomic species with a threefold potential barrier for the internal rotations of the methyl groups. It is expected to be extremely small because of the very large distance of the two methyl groups from each other and the central triple carbon–carbon bond with cylindrical symmetry. The ESR spectrum of 2-butyne radical cation on ZSM-5 at 150 K consisted of seven lines with 10.0-G separation (Fig. 3). It is assigned to two equivalent methyl groups rotating almost freely inside the two-dimensional channels of the ZSM-5 solid catalyst. Perhaps, the anomalously large linewidths observed (4 G) are characteristic of this radical cation with degenerate ground vibronic states (the Jahn–Teller effects) (6). The ESR spectrum of chemisorbed 2-butyne radical cation changed with increasing temperature. Above the normal boiling point of the neutral 2-butyne molecule (27°C at 1 atm), the ESR spectrum changed into nine lines with 6.60-G separation and a g value of 2.0029, which did not change at higher temperature up to 477 K.
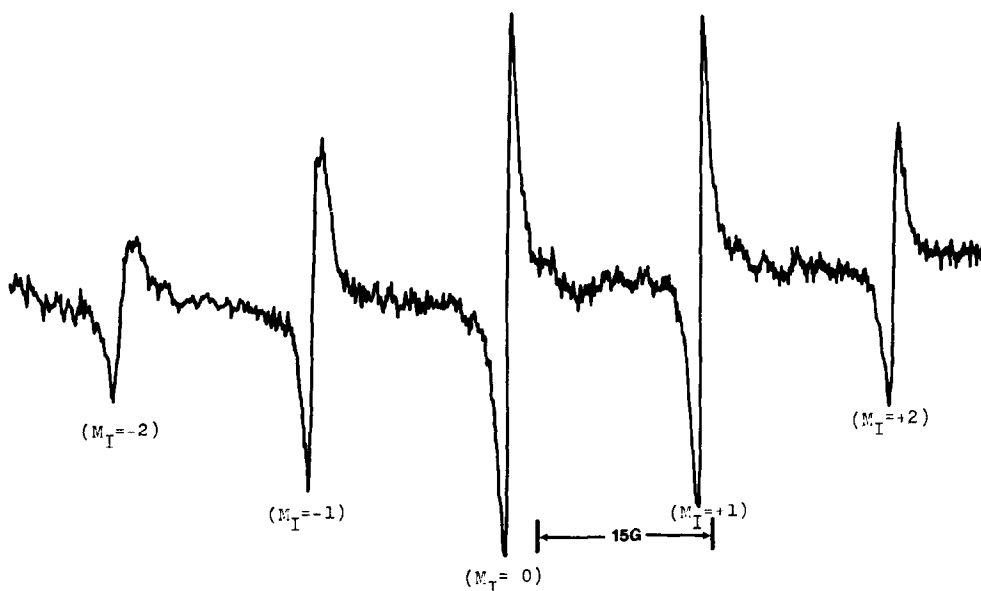
FIG. 2. ESR spectrum of 2,3-dimethyl-2-butene cation on ZSM-5 surface at 330 K.

DISCUSSION

Radical ions have been prepared by various techniques in solution, but these have been generally limited to organic molecules with ionization energy less than 9.0 eV (7). Attempts to prepare the less stable radical cations of alkene and alkynes have been relatively difficult. It is the geometric structures of these radical cations and their interactions with the zeolitic surface which are most crucial to understanding the mechanism of catalytic reactions and radical polymerization on the surface.

In this paper, we report the isomerization of an alkene radical cation and the first alkyne radical cations and their trimerization reaction directly observed on the zeolitic surface by use of ESR techniques. The zeolite ZSM-5 is well known to be technologi-
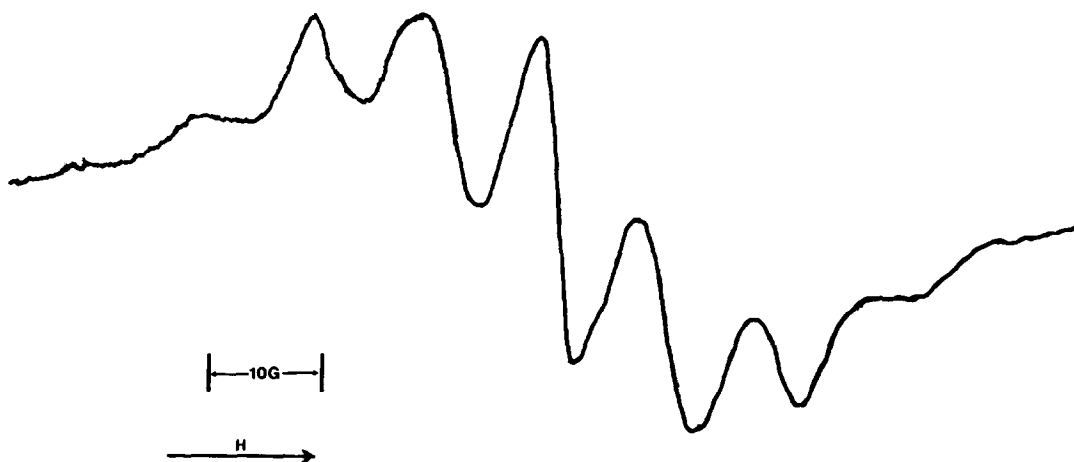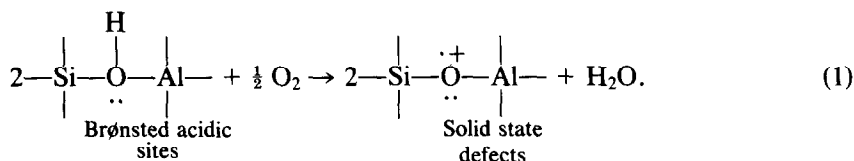

FIG. 3. ESR Spectrum of 2-butyne radical cation on ZSM-5 zeolite surface at −125°C.

cally important in syn-gas and methanol conversion processes (8).

ZSM-5 solid consists of a tetrahedral silica–alumina network with two-dimensional channel structures. In order to preserve the electrical neutrality, either proton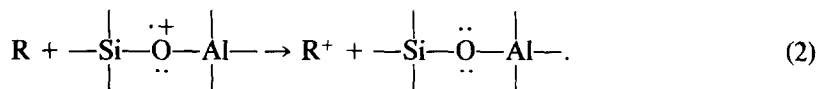s or other cations are bonded to the oxygen atoms of the zeolitic surface. During calcination of H-ZSM-5 catalyst in either air or diluted oxygen atmosphere at 500°C or higher temperatures, the following chemical reaction should be expected to take place on the surface:

$$2-\overset{\displaystyle |}{\underset{\displaystyle |}{Si}}-\overset{\displaystyle H}{\underset{\displaystyle \cdot\cdot}{O}}-\overset{\displaystyle |}{\underset{\displaystyle |}{Al}}- \; + \; \tfrac{1}{2}O_2 \rightarrow 2-\overset{\displaystyle |}{\underset{\displaystyle |}{Si}}-\overset{\displaystyle \cdot +}{\underset{\displaystyle \cdot\cdot}{O}}-\overset{\displaystyle |}{\underset{\displaystyle |}{Al}}- \; + \; H_2O. \qquad (1)$$

Brønsted acidic sites   Solid state defects

The solid-state defects are positive holes on oxygen atoms of the zeolitic or silica–alumina surface. The unpaired electron occupied a nonbonding molecular orbital of the oxygen atom since there is no nuclear hyperfine splittings from the aluminum atom detected at 77 K; furthermore, the g value 2.0092 observed on the ZSM-5 surface is almost identical to isoelectronic holes ($g = 2.010$) produced by X-ray-irradiated silicate glass (9) and borate glass (10), both of these ESR studies being primarily associated with the oxygen atoms of either SiO_4^{3-} or BO_4^{4-} tetrahedra.

The localized nature of the electron on the solid-state defect will interact with the ionizable organic molecule adsorbed on the zeolitic surface. It is worth knowing the energy of formation of the solid-state defects and its fate in the presence of molecular species. Since both silicon atom (E.N. = 1.8) and aluminum (E.N. = 1.5) atom have lower electronegativity (E.N.) than hydrogen atom (E.N. = 2.1) (11), the energy needed to generate such localized solid-state defects is equivalent or similar to that required to remove the electron from the nonbonding orbital of an oxygen atom in a water molecule. Photoelectron studies in the gas phase suggest that it corresponds to the adiabatic ionization potential (I.P.) (12.61 eV) of the nonbonding lone-pair orbital (12). Thus, the solid-state defects on the zeolitic surface are highly energetic so that any organic molecules such as CH_3OH (I.P. = 10.85 eV), C_2H_4 (I.P. = 10.50 eV), and C_2H_2 (I.P. = 11.41 eV) (13) with ionization energy less than 12.61 eV will give an ESR signal by the charge transfer mechanism (14):

$$R + -\overset{\displaystyle |}{\underset{\displaystyle |}{Si}}-\overset{\displaystyle \cdot +}{\underset{\displaystyle \cdot\cdot}{O}}-\overset{\displaystyle |}{\underset{\displaystyle |}{Al}}- \rightarrow R^+ + -\overset{\displaystyle |}{\underset{\displaystyle |}{Si}}-\overset{\displaystyle \cdot\cdot}{\underset{\displaystyle \cdot\cdot}{O}}-\overset{\displaystyle |}{\underset{\displaystyle |}{Al}}-. \qquad (2)$$

Several possible and irreversible chemical pathways for the unstable organic radical cations exist. Two of them are either intramolecular rearrangement (isomerization) into a more stable isomeric radical cation or polymerization with other neutral species; other reactions such as those to generate carbonium ion (14) and ring opening of the conjugated radical cation system have been reported in the literature (15).

On the basis of our experimental data, we proposed the following isomerization for

chemisorbed 3,3-dimethyl-1-butene radical
cation on the zeolitic surface:

$$
\text{(3)}
$$
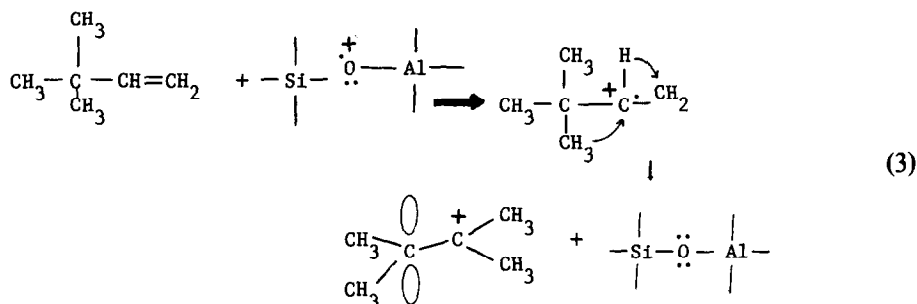
This isomerization reaction is extremely fast even at 123 K as indicated in Fig. 1b.

For the chemisorbed 2-butyne radical cation, the orientation-dependent spin-rotation coupling and the bending vibrations of the two methyl groups should lift the electronic double degeneracy in the ground vibronic state of the radical cation. The major effect of removal of an electron from the neutral molecule would be to lower the out-of-plane bending frequencies a considerable amount for the 2-butyne molecule, where $\nu_{16}(E') = 213$ cm^{-1} and $\nu_{12}(E'') = 144$ cm^{-1} (16), so that the unstable radical cation could be deformed into such a conformation that trimerization reaction would take place between 173 and 300 K (Fig. 4):

$$
\text{(4)}
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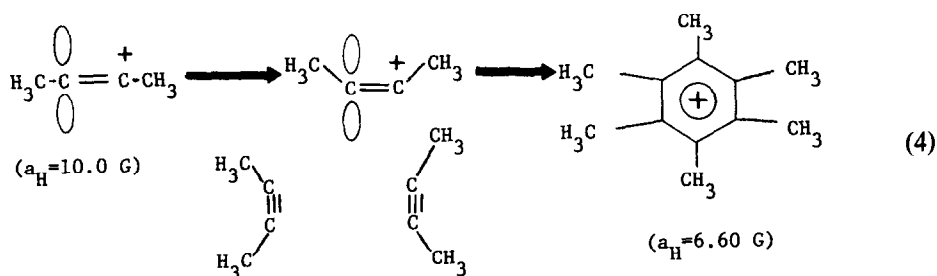
This reaction is further facilitated by the steric restriction of both the radical cation and the two neutral 2-butyne molecules inside the channels of the zeolite, where the radius of the circular- or elliptic-shape cylinder is about 6 Å (17). Other evidence from irreversible changes in ESR spectrum, g value, and the hyperfine splittings of identical methyl groups is consistent with an early reported ESR spectrum of hexamethylbenzene radical cation on mordenite (18).

CONCLUSION

Isomerization of an alkene radical cation and aromatization of an alkyne radical cation on the ZSM-5 solid have been studied on the zeolitic surface by use of electron spin resonance techniques. Changes of ESR spectra with both temperature and time are indications that these chemical transformation events occurred on the zeolitic surface.
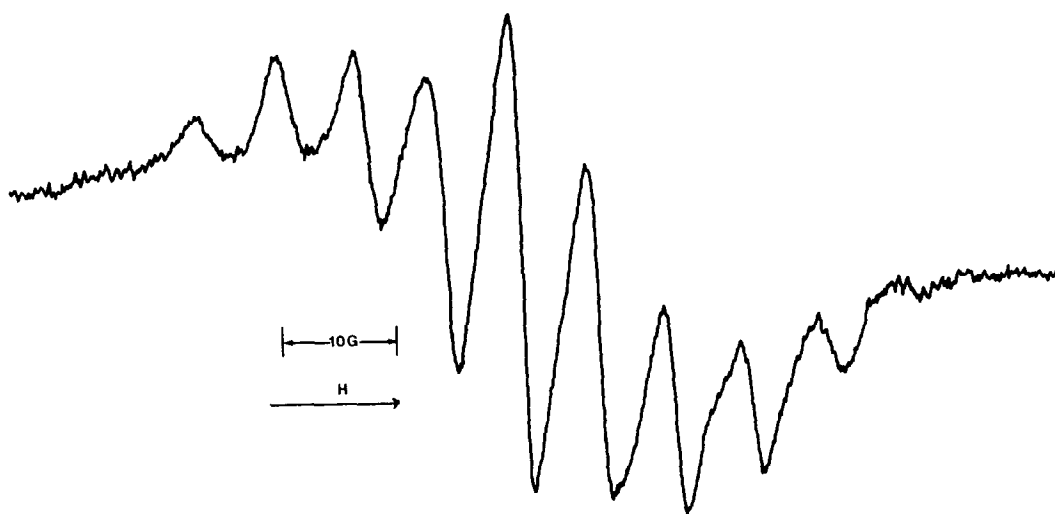
On the basis of these experimental mea-

FIG. 4. ESR spectrum of 2-butyne cation aromatization on ZSM-5 zeolite surface at 310 K.

surements and further information from photoelectron spectroscopic studies, both solid-state defects and radical cations should play an important part in our understanding of initial chemical reactions on both zeolitic and silica–alumina surfaces.

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