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Formation of *trans*-Polyacetylene on Transition Metal Zeolites: A Resonance Raman Study

Acetylene readily polymerizes to form *trans*-polyacetylene on Co(II) and Ni(II) exchanged zeolites. Cu(II), Mn(II), and Zn(II) would not catalyze the formation of the polymer. In order for the catalytic system to be active, Lewis acid sites provided by the aluminum atoms of the framework were also necessary. Resonance Raman spectroscopy provided a sensitive probe for detecting polyacetylene and determining its structure. © 1988 Academic Press, Inc.

INTRODUCTION

There is much interest in electron transfer through the unique channels and cage system of aluminosilicate zeolites and clays. Electrodes made of such materials have been prepared and studied (*1*, *2*). The discovery of electrically conducting organic polymers is an exciting development in the materials research area (*3*). Polyacetylene, which can be readily converted to a conductor by treatment with oxidizing and reducing agents, has been extensively studied (*4*). Its instability under ambient conditions and lack of processability have led to preparations of polyacetylene blends with other matrices (*5*).

In this preliminary study, we have examined the formation of polyacetylene on zeolite surfaces. A series of transition metal ion-exchanged zeolites were examined as catalysts. The sensitivity of resonance Raman spectroscopy was exploited to obtain information on the structure of the polyacetylene formed on the zeolites.

Hendra and co-workers have reported on the formation of polyacetylene on zeolite K–X and Al_2O_3 activated at high temperatures (*6*). No other studies of polyacetylene on zeolites have been reported.

EXPERIMENTAL

The zeolites used in this study were synthesized from silicon (DuPont Ludox TM 40) and aluminum (powder, Alfa) sources according to published procedures (*7*). The transition metal ions were exchanged into the Na zeolites from either chloride or acetate solutions at neutral pH. The zeolite sample integrity was checked by powder diffraction measurements.

Acetylene was purified by passing through a dry ice–acetone slurry. The zeolites were activated in a greaseless vacuum system at pressures of 1×10^{-5} Torr at varying temperatures. After exposure of the zeolite to acetylene vapor for a period of 5 min, the excess acetylene was pumped off.

Raman spectra were obtained by excitation with an argon ion laser (Spectra Physics) or a krypton ion laser (Coherent). The scattered light was collected and filtered through a Spex 1403 double monochromator and detected by a C 31034 GaAs PM tube. The slitwidths were typically 6 cm^{-1} and scan times of 1–3 s/cm^{-1} were used.

Elemental analysis (Na, Si, Al, transition metals) was done with a JEOL JXA-35 electron microprobe using zeolite A as standard. Typically, about 50–60% of the sodium ions in the zeolite framework were replaced by the transition metal ions.

RESULTS AND DISCUSSION

The most extensively used catalysts for the polymerization of acetylene include the Ziegler–Natta catalysts, based on titanium

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alkoxides and alkylaluminum compounds (*8*). Another catalytically active system, first proposed by Lutinger, is made up of cobalt and nickel salts in the presence of a borohydride reducing agent (*9*). The mechanism of action of these catalytic systems is an active area of research. In general terms, it appears that the acetylene binds to the transition metal ion, at the center of which the polymerization proceeds. The Lewis acid is necessary to activate the metal ion–acetylene complex (*10*).

Binding of acetylene to transition metal ions in zeolites has been studied by a variety of spectroscopic techniques (*11–13*). For CoNaA, diffuse reflectance spectroscopy in the *d–d* transition region demonstrated that acetylene was π-bonded to the cobalt ions (*11*). Single-crystal X-ray diffraction showed that the cobalt ions in the α-cages of zeolite A were symmetrically π-bonded to acetylene molecules (*12*). These studies clearly demonstrate that acetylene can act as a ligand to transition metal ions held to the zeolite framework.

Zeolites are also known to contain Lewis acid sites (*14*) arising from framework aluminum atoms and in combination with the transition metal ions can function as polymerization catalysts. We studied the reaction of acetylene with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) exchanged Y zeolites. The zeolites were activated by degassing at 1×10^{-5} Torr for 2 h at temperatures ranging from room temperature to 500°C, cooled to ambient temperature, and then exposed to acetylene vapor. We have used resonance Raman spectroscopy as a probe to study the formation of polyacetylene. Both *cis* and *trans* forms of polyacetylene exhibit strong and broad π–π^* absorption bands ($\varepsilon \sim 10^5$–10^6 cm^{-1}) in the ultraviolet–visible region (*15*). In *cis*-polyacetylene a vibronic structure is observed around 600 nm, whereas a broad, unstructured peak at 700 nm is observed in the *trans* form. Because of the large oscillator strengths of these bands, significant resonance enhancements of Raman bands are observed (*16*). Also, the *cis* and *trans* forms have characteristic vibrational bands and can be readily distinguished. In the *trans* form, strong bands at ~1100 and ~1500 cm^{-1} are observed, whereas, in the *cis* form, bands at 920, 1262, and 1552 cm^{-1} are observed (*17*).

No evidence of polyacetylene was found in the room temperature degassed samples of the transition metal ion zeolites. Upon activation at 50°C, Raman bands characteristic of *trans*-polyacetylene were found on the CoY and NiY samples, but not on the MnY, CuY, and ZnY samples. Such was the case for all temperatures of activation up to 500°C. Only Co(II) and Ni(II) catalyzed the formation of polyacetylene. Figure 1 shows the Raman spectrum of NiY and ZnY, activated at 500°C and exposed to acetylene at room temperature. Bands at 1015, 1140, 1300, and 1560 cm^{-1} in NiY are characteristic of *trans*-polyacetylene. Since the *cis* form of the polymer readily converts to the *trans* form upon heating (*17*), many precautions were taken during the Raman experiments to limit thermal damage. Laser powers at the sample were varied between 1 and 10 mW and samples were spun in an anaerobic spinning cell. Infrared spectroscopy, which can also distinguish between

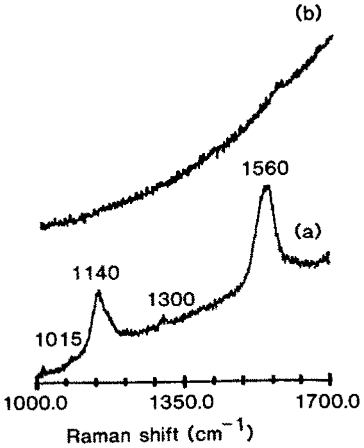

FIG. 1. Resonance Raman spectra of zeolite Y samples activated at 500°C and exposed to acetylene at room temperature: (a) NiY, (b) ZnY. Laser excitation –406.7 nm.

the *cis* and the *trans* forms could not detect the formation of polyacetylene because of the low loadings. The yield of polyacetylene was determined gravimetrically. In the case of CoY zeolites, the best yields were about 5–10% by weight.

To examine the role of the zeolite framework, we studied a series of Co(II)-containing materials including $CoCl_2$-impregnated silica gel, Co(II) ion-exchanged amorphous aluminosilicate solid, CoNaA, CoNaY, CoNaX, and CoNaZSM-5. These materials were degassed at 100°C, cooled to room temperature, and exposed to acetylene vapor. Except for the silica gel sample, *trans*-polyacetylene was formed on all of the other samples. Clearly, Lewis acid sites originating from aluminum atoms are required for polymerization. Because of the small yields, quantitative comparison of the formation of polymer on the various materials was difficult. The resonance Raman intensities are also an indicator of the extent of polymerization. Based on these intensities, it appears that the Co(II) zeolites are considerably more effective at polymerizing acetylene than the Co(II) amorphous aluminosilicate solid.

The Raman bands also provide structural information on the *trans*-polyacetylene formed on these materials. Figure 2 shows the Raman spectrum of polyacetylene formed on a CoNaY sample (activated at 100°C) taken at different excitation wavelengths. Peaks of the Raman bands shift progressively to higher wavenumbers at higher excitation energies. This phenomenon is characteristic of *trans*-polyacetylene and arises because the polymer is formed of many subunits of differing chain lengths of *trans* sequences (*18*). At higher excitation energies, resonance with smaller units of *trans* sequences occur, and, as expected from the characteristic vibrational spectra of polyenes (*19*), the Raman frequencies shift to higher energies. The two strongly enhanced Raman bands have been assigned to predominantly C–C stretches, containing contributions from both double- and single-bond stretching motions (*18*). Many empirical relations have been developed between the frequencies of these bands and the number of alternating double bands present in the polyacetylene backbone (*20*). The frequency at 1569 cm^{-1} taken at 413.1 nm would correspond with five to six C=C bonds in a defect free arrangement. The frequencies observed in this study (Fig. 2) are typical of *trans*-polyacetylene made with Ziegler–Natta catalysts. However, for Ziegler–Natta polymerized acetylene, strong enhancement of Raman bands is also observed upon excitation with 647.1 nm radiation. In the zeolite-based samples, no enhancement was observed at this red wavelength, indicating that the polymer does not contain a significant fraction of longer conjugated C=C units ($N_{C=C} \sim 50$ units or larger) (*16*).

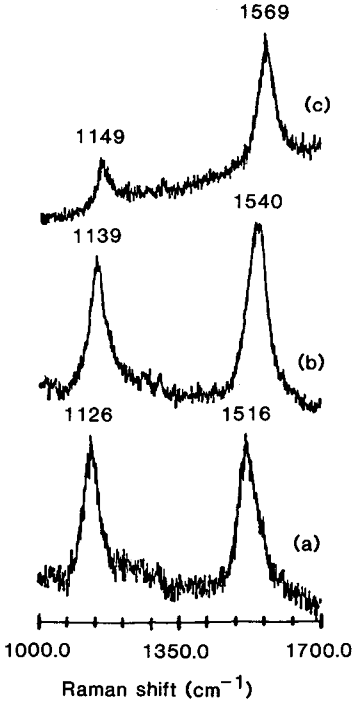

FIG. 2. Resonance Raman spectra at varying excitation wavelengths of CoY samples activated at 100°C and exposed to acetylene vapor at room temperature: (a) 514.5 nm, (b) 457.9 nm, (c) 413.1 nm.

The ability of only Co(II) and Ni(II) ions to catalyze the polymerization reaction is in agreement with the results in the literature regarding studies of trimerization of acetylene on transition metal zeolites (*21*). The back bonding ability from the metal *d*-orbitals in the case of Co(II) and Ni(II) was considered important in the activation of acetylene (*12, 21*). We did not detect the presence of benzene in our vibrational studies. The diffuse reflectance spectrum of acetylene on CoNaA showed a broad, unstructured background absorption, which was assigned to the extensive charge transfer interaction of acetylene with Co(II) ion (*11*). This study indicates that this featureless absorption arises from *trans*-polyacetylene formed on the zeolite.

Whether the polymer is formed in the cages of the zeolites or on the surface is still in doubt. It is likely that it is forming on the surface since zeolites with very different cage and channel dimensions, such as A, Y, and ZSM-5, all form *trans*-polyacetylene of similar structure. The requirements of polymerization include the presence of Co(II) and Ni(II) ions with vacant coordination sites and aluminum Lewis acid sites probably in close proximity. The low yields of the polymer could arise from blockage of these catalytic sites by polyacetylene, thus impeding further polymerization. The synthetic challenge is to polymerize acetylene inside the linear cavities of zeolites such as ZSM-5 or ZSM-11 instead of on the surface and is presently under investigation.

In summary, it appears that Co(II) and Ni(II) exchanged aluminosilicates can catalyze the polymerization of acetylene. Zeolitic frameworks tend to promote the polymerization as compared to amorphous aluminosilicates. Also, the *trans*-polyacetylene formed on the zeolite is built up of shorter segments of conjugated C=C bonds as compared to the conventional Ziegler–Natta catalysts.

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PRABIR K. DUTTA[1]
M. PURI

Department of Chemistry
The Ohio State University
Columbus, Ohio 43210

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[1] To whom correspondence should be addressed.