

RESONANCE RAMAN SPECTROSCOPIC STUDY OF CATION RADICALS OF AROMATIC MOLECULES FORMED IN THE INTERLAYER OF TRANSITION-METAL EXCHANGED MONTMORILLONITES

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ABSTRACT Resonance Raman spectroscopy has been demonstrated to give important structural information on the reactions of aromatic molecules in the interlayer of transition-metal ion-exchanged montmorillonites. Para-substituted benzenes or 4,4'-substituted biphenyls are oxidized to form their cation radicals, which are stabilized in the interlayer of the clay mineral. The oxidative dimerization or polymerization results in the formation of biphenyl type cations and poly-p-phenylene cations from mono-substituted benzenes and benzene, respectively.

1. INTRODUCTION

Montmorillonite, a layered clay mineral, shows interesting behavior in the adsorption of organic molecules due to the presence of interlayer space containing exchangeable metal cations which compensate the positive charge deficiency in the aluminosilicate sheet. Various kinds of aromatic molecules are adsorbed in the interlayer of montmorillonite, replacing water molecules which surrounds exchangeable metal cations in the interlayer(1).

Mortland, Pinnavaia and their co-workers have found that the adsorption of certain aromatic molecules on montmorillonites whose exchangeable cations are saturated with transition metal ions leads to the formation of colored complex(2-4). The IR spectrum of benzene complex formed under a dry atmosphere indicates the chemical state of the adsorbed benzene is remarkably different from that of liquid benzene (2,3), while adsorbed anisole is reported to dimerize to 4,4'-dimethoxybiphenyl(5). The essential step in the formation of these colored complexes has been shown to involve an electron transfer from the adsorbed organic molecules to the interlayer transition-metal ion, notably by ESR(4,6). However, the detailed spectroscopic information concerning the structure of adsorbed species have not been sufficient.

In order to understand the structure and the nature of these colored compounds, largely benzene derivatives, we investigated the adsorption of these aromatic molecules on transition-metal, Cu(II), Fe(III), Ru(III) ion-exchanged montmorillonites using resonance Raman

spectroscopy.

Resonance Raman spectroscopy can give the spectrum of the objective species only, even if the sample to be studied has a complex composition by selecting the excitation wavelength of laser light. Therefore, determination of the structure of adsorbed species from resonance Raman spectra can be more straightforward than in the assignment of IR spectra complicated with the presence of several adsorbed species and interfered with the absorption of clay mineral itself.

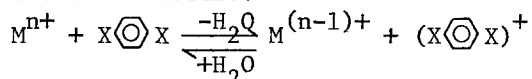
2. PROCEDURE OF ADSORPTION

Transition-metal ion-exchanged montmorillonites were prepared by suspending native montmorillonite in aqueous solution of metal salt(2), separated by centrifuging, washed and freeze-dried.

The organic adsorbate in a small vessel was put into a phosphorous oxide desiccator and its vapor was allowed to adsorb on the clay at room temperature. When the adsorbate was solid, a clay sample was immersed into the cyclohexane solution and dried in the desiccator. In the adsorption of pyridine, barium oxide was used as a drying agent. The formation rate of colored complexes was dependent on the adsorbate molecules and the dryness of montmorillonite. In the case of anisole or phenol, the color began to appear at once when the adsorbate was brought into contact with the dried montmorillonite, but it took about two weeks to finish the reaction in pyridine adsorption.

3. ADSORPTION OF PARA-SUBSTITUTED BENZENES AND 4,4'-SUBSTITUTED BIPHENYLS(7,8).

p-Dimethoxybenzene adsorbed on Cu-montmorillonite under a dry condition forms yellow complex. The absorption spectrum and the resonance Raman spectrum of the complex correspond respectively to those of p-dimethoxybenzene cation radical in solution(7). At the same time, cupric ion in the interlayer is reduced to cuprous ion. Thus the following reaction occurs in the interlayer of montmorillonite, reversibly, depending on the ambient moisture.



Similar reactions are observed in the adsorption of p-xylene and p-dichlorobenzene.

In the adsorption of 4,4'-dimethoxybiphenyl(abbreviated as 4,4'-DMOBP hereafter), dark green colored complex is formed(8). The absorption spectrum of this complex, as shown in Figure 1e, almost coincides with that of 4,4'-DMOBP cation radical in freon matrix(9). Raman spectra of this complex excited at the wavelengths in resonance with these two absorption bands are shown in Figure 2. The intensity distribution of Raman spectra of this complex is similar to that of biphenyl anion, which is also shown in Figure 2 by lines(10), except for CO stretching band of DMOBP around 800 cm^{-1} . Accordingly the cation radical of 4,4'-

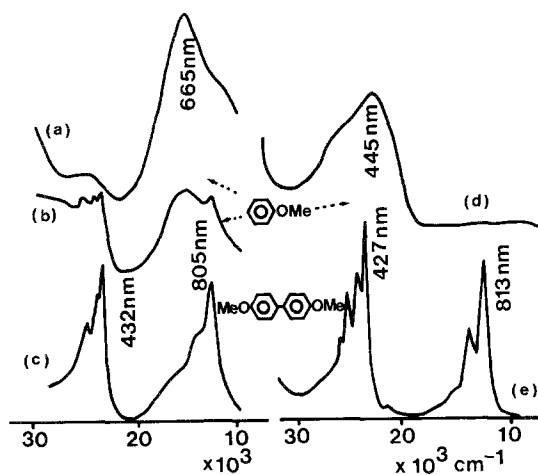


Figure 1. Absorption spectra of anisole and 4,4'-dimethoxybiphenyl adsorbed on Cu-montmorillonite(a,b,c) and spectra of anisole and 4,4'-dimethoxybiphenyl cation radicals formed in freon matrix(d,e)(9).

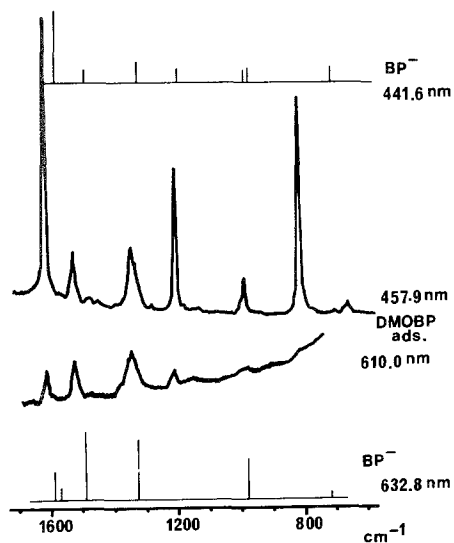


Figure 2. Resonance Raman spectra of 4,4'-dimethoxybiphenyl adsorbed on Cu-montmorillonite with 457.9 and 514.5 nm excitation, and those of biphenyl anion radical in THF solution with 441.6 and 632.8 nm excitation (10).

DMOBP is formed similarly with the case of para-substituted benzenes. The Raman spectra of biphenyl type cation radicals are characterized by the evident high frequency shift of the inter-ring CC stretching band compared with that of neutral molecules (in the case of 4,4'-DMOBP cation in the interlayer, 1282 cm^{-1} to 1343 cm^{-1}).

4. ADSORPTION OF MONO-SUBSTITUTED BENZENES(8).

The color of the adsorption complex of anisole on Cu-montmorillonite is dark blue and the absorption spectra are different from the spectrum of anisole cation radical but looks more like that of 4,4'-DMOBP cation as shown in Figure 1. The Raman spectrum with 610.0nm excitation consists of the bands corresponding to those of 4,4'-DMOBP cation. On the other hand, the spectrum with 457.9nm excitation has another set of bands in addition to bands due to 4,4'-DMOBP cation, which is considered to be due to anisole cation. The ratio of these two species depends on the adsorption condition or the amount of cupric ion in the montmorillonite as shown in Figure 3.

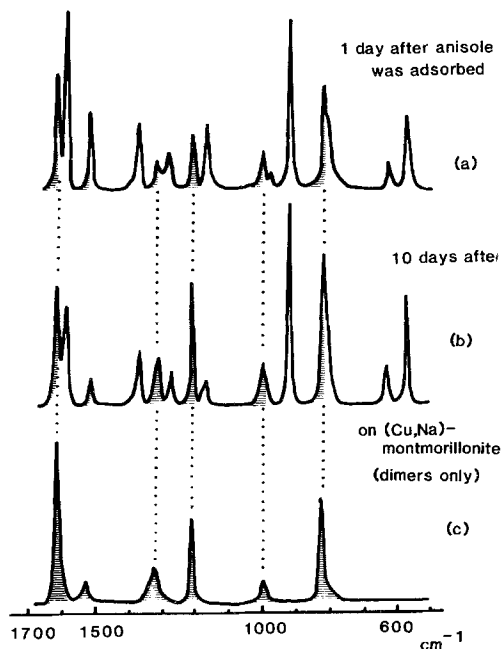
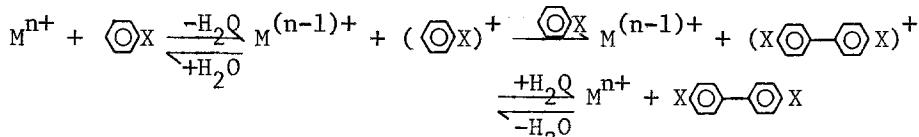


Figure 3. Resonance Raman spectra of anisole adsorbed on Cu-montmorillonite with 457.9nm excitation. Dependence on the adsorption conditions. In each spectrum background due to a broad emission band was subtracted.

The following reaction is considered to occur in the adsorption of anisole, which is consistent with the mechanism proposed by Fenn et al (5).



The similar reactions are observed in the adsorption of some mono-substituted benzenes, such as chlorobenzene or fluorobenzene adsorbed on Fe-montmorillonite, although the amount of biphenyl type cation formed is less.

The formation of biphenyl type cation from mono-substituted benzene cation is distinguished by the inter-ring CC stretching Raman band around 1350 cm⁻¹ which is not observed in benzene-type cations, and at the same time the electronic absorption band in the range of 500 to 700nm is also a diagnosis of the existence of biphenyl type cation radical.

5. ADSORPTION OF BENZENE, BIPHENYL AND p-TERPHENYL(11).

Benzene adsorbed on Fe- and Cu-montmorillonite in a dry atmosphere forms a red colored complex(type II)(3,4) and the absorption bands of this complex appear around 500nm and in infrared region. Contact with water vapor converts this complex to type I complex(3,4) reversibly, which has the absorption around 400nm. The absorption spectra and

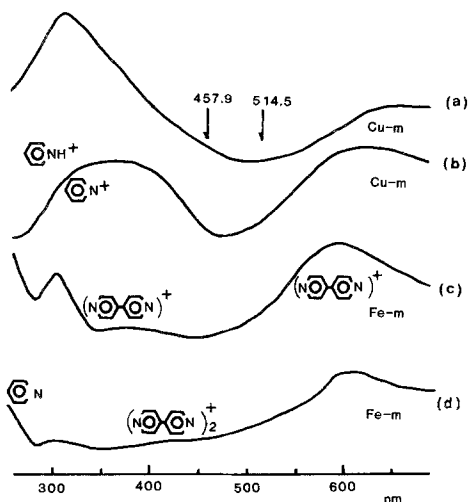
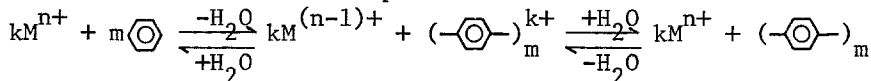


Figure 4. Absorption spectra of pyridine adsorbed on Cu- and Fe-montmorillonites which were ion-exchanged in acidic solution(a,c) and in neutral solution(b,d).

resonance Raman spectra of type I and type II complexes correspond respectively to those of neutral poly-p-phenylene and poly-p-phenylene cation. Thus, polymerization through cation radical occurs in the adsorption of benzene accompanied with the reduction of metal ions in the montmorillonite at room temperature.



Biphenyl and p-terphenyl react similarly to form poly-p-phenylene cation, although the adsorbed amounts are less compared with that of benzene.

6. ADSORPTION OF PYRIDINE.

Pyridine is adsorbed not only in the interlayer, but also on the edge or the surface of the clay, bonding with Brønsted or Lewis acid sites. Thus several kinds of adsorbed species are observed in the absorption spectra of pyridine adsorbed on Cu- and Fe-montmorillonites as shown in Figure 4 with tentative assignments; physically adsorbed pyridine, pyridinium ion, 4,4'-bipyridyl cation and its dimer

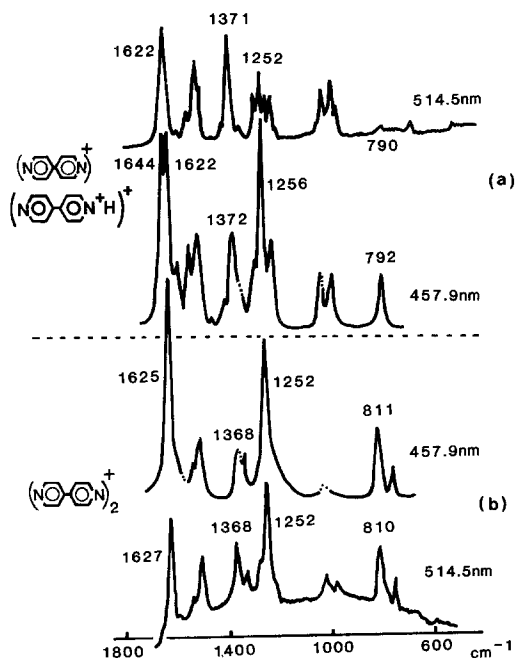


Figure 5. Resonance Raman spectra of pyridine adsorbed on Fe-montmorillonites with 457.9 and 514.5nm excitation.

cation. However, protonated bipyridyl type species may co-exist. As in the biphenyl-type cation, the absorption bands around 600nm are characteristic of bipyridyl type cation. Methylviologen mono-cation radical is known to have the corresponding absorption band(12). Relative amounts of the adsorbed species mentioned above depend on the preparation condition of ion-exchanged montmorillonite. On a Fe-montmorillonite ion-exchanged in acidic solution(pH 3), a large amount of pyridinium ion is observed while the amount of bipyridyl cation formed is scarce.

4,4'-Bipyridyl cation and its dimer cation are identified from the resonance Raman spectra with 457.9 and 514.5nm excitation, shown in Figure 5. The inter-ring CC stretching band around 1370 cm^{-1} characteristic for bipyridyl type is observed in all these spectra, while Raman bands of pyridine or pyridinium ion around 1000 cm^{-1} are weak in these spectra. The upper spectra(Figure 5a) are similar to those of methylviologen mono-cation radical, $(\text{MeN} \text{---} \text{---} \text{NMe})^+$ (12), but very complicated. The spectra are attributed to the mixture of two kinds of 4,4'-bipyridyl cation, and one would have the interaction with proton which comes from pyridinium ion or the Brønsted acid site. Bipyridyl dimer cation may have an absorption band around 450 to 500nm(13), thus the fact that the Raman spectra excited at these two wavelengths are the same as seen in Figure 5b, is consistent with the presence of the dimeric species.

Molecules which have been studied are arranged in Figure 6, according to their ionization potentials and their reactions. Molecules be-

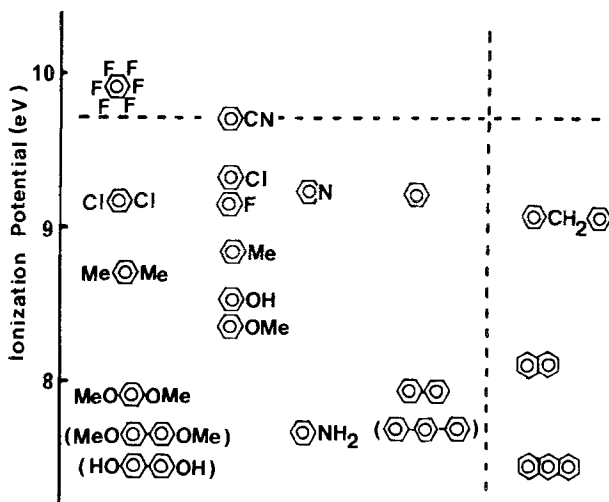


Figure 6. Ionization potentials of aromatic molecules, grouped according to their behavior of adsorption on transition-metal ion-exchanged montmorillonites.

low and to the left side of the dotted lines are observed to form cation radicals in the interlayer. Molecules to the right side of the dotted line are too rigid and/or bulky to be adsorbed. Hexafluorobenzene is adsorbed considerably, but its ionization potential is too high to form the cation. These reactions depend also on the oxidizing power of the interlayer metal cation(4), and the reactivity of Fe(III) or Ru(III) ion for radical formation is observed to be higher than that of Cu(II) ion.

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