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FT-IR spectroscopic studies of metal nitrates supported on a modified montmorillonite clay

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Diffuse reflectance FT-IR spectra of transition metal nitrates on a modified montmorillonite clay show strong absorptions due to the presence of NO^+ and NO^- ions. An attempt has been made to explain the mechanism of activation of the metal nitrates by the clay.

Keywords: Supported catalysts; montmorillonite clay; metal nitrate; ions

1. Introduction

Montmorillonite clays belong to the group of 3-layer minerals and are distinguished, among other things, by the large number of exchangeable ions. Exchange with hard high charged ions like Al^{3+}, Fe^{3+}, Cu^{2+}, H^+, etc., induces a high degree of catalytic activity.

The characteristic properties of the mineral montmorillonite are of decisive importance for their catalytic action in many organic reactions. This clay belongs to the group of acid catalysts because of its function and chemical constitution and is distinguished by a highly selective catalytic activity. It is generally used in reactions which are otherwise catalysed with Bronsted acids or the so-called Lewis acids. Compared to these acids, the montmorillonite catalyst acts as a proton (or Lewis acid site) donor within the microenvironment of the silicate sheet and the reactants are conveyed to the active catalytic site by diffusion processes, the products being removed in a similar way. Cation exchanged natural montmorillonite has been used to catalyse a variety of organic reactions [1] namely, alkylation of phenols [2], Friedel-Craft's acylation of aromatic hydrocarbons [3], ester or ether production by direct addition of either carboxylic acids or alcohols to alkenes [4], selective reduction of nitroarenes [5],

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oxidative rearrangement of alkyl aryl ketones with thallium trinitrate [6], alkoxylation and acetalisation of unsaturated aldehydes [7], oxidation of secondary alcohols to ketones and of benzoins to benzils [8,9], formation of new bonds [10], etc. They have also been used as microagents for unusual chemical synthesis [11].

Adsorption of transition metal nitrates on clays not only induces changes in their reactivity but also simplifies commonly encountered work up and isolation problems of conventional methods of nitration. Laszlo et al. [12], have reported nitration using transition metal nitrates, in particular copper and ferric nitrate impregnated into acidic clays such as modified bentonite or montmorillonite clays. It has been found that clay supported nitrates are sources for nitrosonium ions. The presence of these ions has been proved by experimental techniques [12]. Even then, the exact nature of the species present on the clay surface and the mechanism of their generation is not known. One of the best methods of investigating this aspect is surface FT-IR spectroscopy [13–15]. Thus, the study was conducted using diffuse reflectance FT-IR spectroscopy. The infrared spectra of a number of clay supported transition metal nitrates as well as lead nitrate have been recorded and the changes in the spectrum of the parent clay on reaction with the nitrates studied.

2. Experimental

PREPARATION OF CLAY SUPPORTED METAL NITRATES

Clay supported metal nitrates were prepared by the procedure of Laszlo et al. [12], as follows:

In a 100 ml pear shaped flask the respective metal nitrate (0.02 mol., dry weight basis) is dissolved in acetone (50 ml). K-10 montmorillonite clay (Sud-Chemie A.G, 4 g) is then dispersed in the solution with vigorous stirring. The solvent is evaporated under reduced pressure (in a rotary evaporator with a water aspirator) on a water bath at 50 °C. After 30 min, the dry solid crust adhearing to the walls of the flask is scraped with a spatula and drying is resumed under the same conditions for another 30 min. This procedure yields about 8 gm of the respective clay supported nitrates as dry powders.

FT-IR SPECTRA

FT-IR spectra were recorded on a Bruker IFS-85 FT-IR spectrometer using a Harrick DRA-2CI diffuse reflectance accessory. Clay supported metal nitrate samples were intimately mixed with fine dry KBr powder and mounted on the accessory. 500 scans at a mirror velocity of 4 were coadded to give a resolution of 2 cm^{-1}. The spectra were not converted into Kubelka Munk Units. Areas

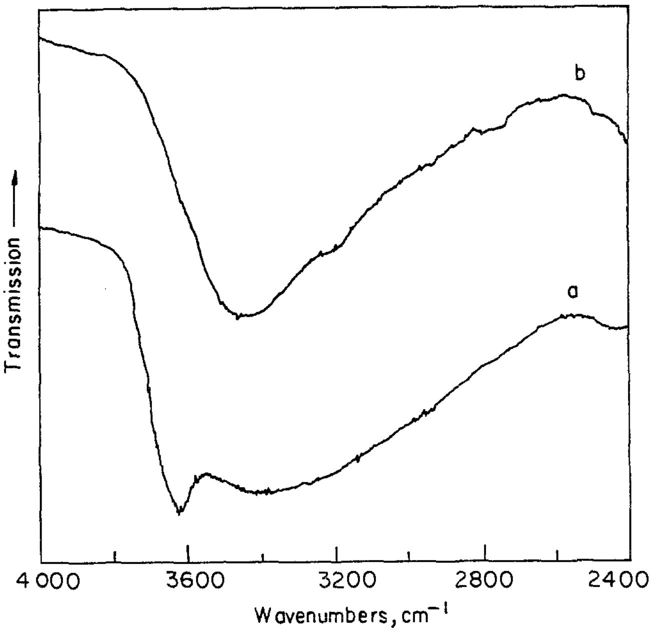

Fig. 1. The 4000–2400 cm^{-1} region in the infrared spectrum of (a) montmorillonite clay; (b) clay supported zinc nitrate.

under the absorption bands were normalised by dividing by the area under the clay absorption band at 1057 cm^{-1}.

3. Results

Fig. 1 (a) shows the 4000 to 3000 cm^{-1} region in the infrared spectrum of montmorillonite clay. A sharp band can be seen at 3628 cm^{-1}. This band is a shoulder on a broad asymmetric band centred at 3400 cm^{-1}. On reaction with zinc nitrate, significant changes can be seen in the spectrum. The shoulder at 3628 cm^{-1} is absent and the broad band shifts to 3435 cm^{-1} (fig. 1b). Similar changes were seen in the spectrum of the clay when reactions were conducted with other metal nitrates except lead nitrate. The frequency position of the broad band for the various clay supported metal nitrates is given in table 1. Fig. 2 shows the 2500 to 2000 cm^{-1} region in the infrared spectrum of clay supported zinc nitrate. A sharp doublet is seen around 2400 cm^{-1}. Except clay supported lead nitrate or pure clay similar doublets were seen in the spectra of all other clay supported metal nitrates. The frequency position of the band is given in table 1. A weak band was seen between 2050 and 2100 cm^{-1} in the spectra of clay supported transition metal nitrates (fig. 2, table 1). A strong band at 1635

Table 1
Frequency position (cm^{-1}) and assignments [a] of IR absorption bands of montmorillonite clay [b] and various transition metal nitrates supported on the clay.

Sample	ν OH	ν OH (H_2O)	δ H_2O	ν^+(NO)	$\nu_a NO_2$	$\nu_a(NO_3^-)$	$\delta(NO_3^-)$
Clay	3630	3400	1635	–	–	–	–
Cobalt nitrate on clay		3460	1617	2439, 2393	2090	1389, 1353	829
Copper nitrate on clay		3430	1620	2422, 2402	2063	1382, 1353	825
do *	3630	3400	1630	2242, 2402	2063	1382, 1353	825
Manganese nitrate on clay		3440	1600	2426, 2397	2097	1380, 1358	825
Nickel nitrate on clay		3430	1623	2414, 2397	2065	1390, 1360	826
Cadmium nitrate on clay		3445	1623	2410, 2397	2052	1388, 1355	832
Zinc nitrate on clay		3435	1625	2430, 2400	2094	1389, 1354	829
Ferric nitrate on clay		3430	1623	2435 2395	2090	1388, 1355	825
Lead nitrate on clay	3630	3400	1635	–		1363	–

[a] ν: stretch and δ: in plane deformation.

[b] The absorption at 1050 cm^{-1} in the spectrum of the clay is due to M M OH bending vibrations.

* After use in a nitration reaction.

cm^{-1} in the spectrum of the clay moves down to lower frequencies on reaction with the transition metal nitrates (table 1). Fig. 3a shows the 1500–700 cm^{-1} region in the infrared spectrum of the montmorillonite clay. The spectrum shows a broad band centred at 1050 cm^{-1}. The spectrum of clay supported zinc nitrate in this region is shown in fig. 3b. The spectrum shows a strong split band at 1389 and 1354 cm^{-1}. The intensity of this band is much stronger than the broad band at 1050 cm^{-1}. A sharp band of medium intensity can be seen at 829 cm^{-1}. Similar bands could be seen for all clay supported transition metal nitrates. The frequency positions of all bands in this region for the clay supported metal nitrates are given in table 1. Clay supported lead nitrate shows a weak band at 1365 cm^{-1} (fig. 3c). The normalised integrated intensities of the 1390, 1355 cm^{-1} band as well as the 830 cm^{-1} band are given in table 2. For the clay supported metal nitrates the intensities of the bands vary as Cu > Ni > Fe > Zn > Co > Mn > Cd > Pb (table 2). After using clay supported copper nitrate in an aromatic nitration experiment, the 3628 cm^{-1} band reappears and the broad OH band moves down to 3400 cm^{-1} (table 1). Also, the intensities of the 1390 cm^{-1} doublet and the 830 cm^{-1} band drop significantly (table 2).

4. Discussion

The sharp 3628 cm^{-1} band in the IR spectrum of the clay has been assigned to the stretch of lattice hydroxyl groups in the octahedral region [16]. The peak is known to be a combination of several absorptions, each individual absorption being due to a lattice OH group situated between a unique pair of octahedral metal ions. On reaction of the clay with the transition metal nitrates, the band disappears probably due to the interaction with ions or molecules which result from the reaction. Similar changes in the OH region were seen when carbon monoxide was adsorbed on to aerosil and the changes were attributed to the formation of an (OH---CO) bond [17]. The 3380 cm^{-1} band in the IR spectrum of the clay is assymetric and is assigned to interlayer water molecules in a variety of environments [16]. The shift of this band to higher frequencies is probably due to a disruption of this hydrogen bonded network by diffusing cations. The absence of diffusion of the bulky Pb^{2+} ions into the clay, could be the reason that the spectrum of clay supported lead nitrate remains unchanged

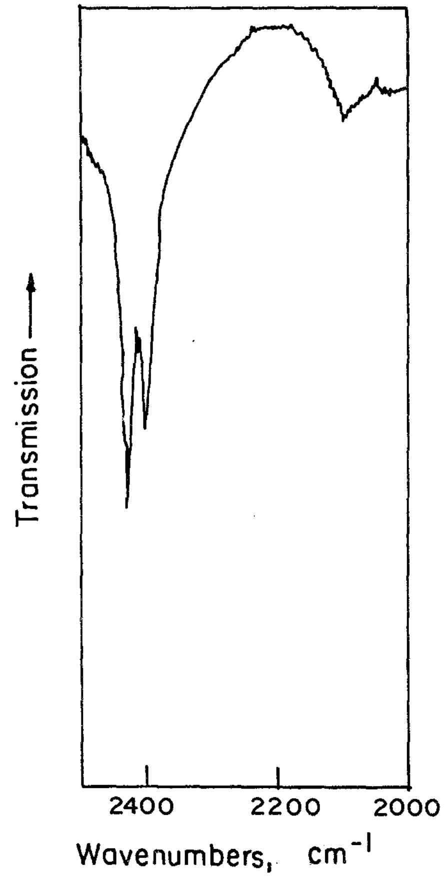

Fig. 2. The 2500–2000 cm^{-1} region in the infrared spectrum of clay supported zinc nitrate.

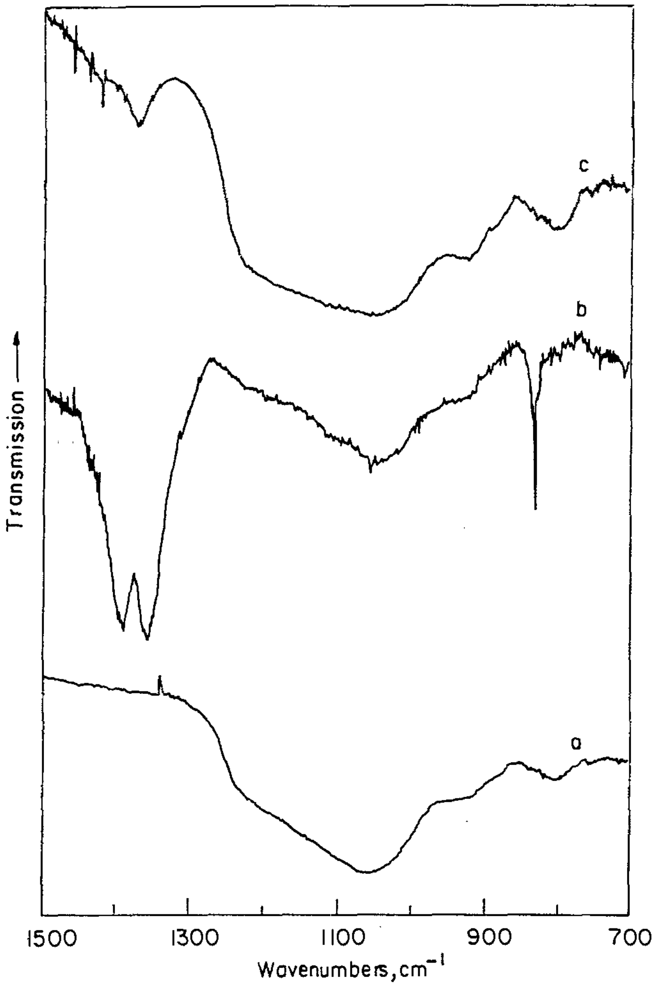

Fig. 3. The 1500–700 cm^{-1} region in the infrared spectrum of: (a) montmorillonite clay; (b) clay supported zinc nitrate and (c) clay supported lead nitrate.

in this region. The shift of the band to higher frequencies could also be a result of changes in the clay structure which leads to changes in the interaction between hydroxyl groups of water molecules and oxygen atoms of two adjacent laminea [13]. The bands appearing around 2400 cm^{-1} are due to nitrosonium ions (fig. 2).

It is known that while anionic NO absorbs around 1195 cm^{-1} the absorption of free NO is around 1876 cm^{-1} [18]. In a compound like $NOVF_6$, the NO group is cationic and absorbs around 2390 cm^{-1} [19]. The bands in the present study being around 2400 cm^{-1} indicate clearly the cationic character of the NO group. Sharp and Thorley [19], have also shown that the NO^+ absorption occurs between 2150 and 2400 cm^{-1}. The band appears as a doublet due to the presence of two differently bonded NO^+ ions on the surface [20]. The absence

Table 2
Normalised integrated intensities of the $\nu_a(NO_3^-)$ and $\delta(NO_3^-)$ bands for various clay supported metal nitrates.

Clay supported metal nitrates	Normalised integrated intensity	
	$\nu_a(NO_3^-)$	$\delta(NO_3^-)$
Cobalt nitrate	0.90	0.09
Copper nitrate	1.12	0.21
do *	0.43	0.09
Manganese nitrate	0.89	0.08
Nickel nitrate	1.10	0.14
Cadmium nitrate	0.74	0.05
Zinc nitrate	0.97	0.12
Iron nitrate	0.98	0.13
Lead nitrate	0.01	0.04

* After use in a nitration reaction.

of bands in this part of the spectrum for clay supported lead nitrate (table 1) indicates negligible concentration of NO^+ ions. A weak band between 2050 and 2100 cm^{-1}, (fig. 2) could be assigned to surface adsorbed NO_2. A huge frequency shift of the NO_2 asymmetric stretch could be occuring due to the loss of an electron to the surface [18]. The NO_2 asymmetric stretch of solid N_2O_4 is at 1752 cm^{-1} [21] and moves up to 2100 cm^{-1} on the surface of zeolites by the same mechanism [20]. It is likely that a N_2O_4 absorption would also be submerged in this weak band around 2100 cm^{-1}. The strong band at 1635 cm^{-1} in the spectrum of the clay (table 1) is due to the deformation vibration of interlayer water molecules [13]. The shift of the band to lower frequencies on reaction with the transition metal nitrates is due to a disruption of the H bonded network of the water molecules caused by diffusing cations. Again clay supported lead nitrate shows no shift in this band indicating absence of diffusion of Pb^{2+} ions into the clay. The broad band at 1050 cm^{-1}, is due to M M OH bending vibrations of the clay [16] (fig. 3a). The strong doublet at 1388, 1355 cm^{-1} (fig. 3b) can be assigned to the asymmetric stretch of NO_3^- ions [22]. The absorption is the degenerate $\nu_3(E')$ mode and appears split due to an asymmetric change in the matrix coefficients of the force constants of the adsorbed ion [13]. The large intensity of the band arises from an increase in the dipole moment of the band brought about by the low symmetry environment of the ion. Forster and Schultz [23] have shown that when deuterium, nitrogen or oxygen was adsorbed into Na A or NaCa A type zeolites they give rise to IR active absorptions by virtue of an induced dipole moment. The sharp, medium intensity absorption at 830 cm^{-1} is the in-plane bending vibration of the NO_3^- ion, the $\nu_2(A_2'')$ mode [22]. This vibration also has an induced dipole moment as evidenced by its appreciable intensity. In the case of clay supported lead nitrate (fig. 3c), the above bands show little or no intensity probably implying that the ions are not adsorbed into cages of the clay.

The normalised integrated intensities of the two absorptions for the various clay supported metal nitrates is an indication of the interaction between the clay and the nitrate ion. The spectrum however does not show any absorption due to the out-of-plane bending mode, $\nu_4(E')$ mode which occurs around 720 cm^{-1} for the NO_3^- ion. The band due to the symmetric stretch of the nitrate ion occuring around 1050 cm^{-1} is masked by the M M OH vibrations of the clay. Thus the present study shows that on adsorption of the metal nitrate on the clay, the metal ions diffuse into the interlayer spaces and replace the protons coordinated to the water molecules. The interlamellar water molecules known to be in a highly ionised state [24] also release protons which interact with the adsorbed NO_3^- ions giving nitric acid. The acid then decomposes to give nitrogen dioxide or N_2O_4 finally leading to the formation of NO^+ and NO_3^- ions. This sequence can be represented as follows:

$$M(NO_3)_2 + H^+(\text{clay}) \rightarrow M^{++}(\text{clay}) + 2NO_3^- + H^+$$

$$HNO_3 + (\text{clay})_{\text{reduced}} \rightarrow NO_2 + (\text{clay})_{\text{oxidised}}$$

$$NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO_3^- + NO^+.$$

4. Conclusion

Diffuse reflectance FT-IR studies on clay supported transition metal nitrates show strong absorptions corresponding to NO^+ and NO_3^- ions. A model is presented for the generation of these ions on the clay surface. This model is based on the diffusion of the metal ions into the clay lattice and the subsequent formation of N_2O_4 that finally leads to the generation of NO_3^- and NO^+ ions.

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