

## Infrared spectral characterization of acidity of zirconium pillared clays

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Received 18 June 1997; revised 14 January 1998

Montmorillonite and vermiculite intercalated with polyoxo cations of zirconium have been prepared. The nature of acidic sites has been studied by infrared (IR) spectroscopy using pyridine and ammonia as the probe molecules. The IR spectral data show three types of acid sites to be available on the pillared clay catalysts. The existence of Brønsted acid, Lewis acid and weak acidic sites has been demonstrated. The effect of heat treatment on the intensities of IR spectral bands has been investigated to confirm the presence of weak acid sites to which pyridine is hydrogen bonded.

Pillared clays are a class of solid acid materials obtained by intercalating polyoxo cations of metals such as aluminium, zirconium, chromium, titanium, iron<sup>1-5</sup>, etc. The resultant materials after calcination contain oxide pillars which prop open the clay sheets and thus expose the internal surface of the clay layers for adsorption and catalysis. In general, pillaring of clays enhances the acidity and the pillars have been assumed to generate Lewis acid sites<sup>6</sup>. Adsorption of bases has been used for the determination of the acidity of solid surfaces<sup>7,8</sup>. Ammonia, pyridine or aliphatic amines are the bases most often used in adsorption measurements<sup>9</sup>. These bases on chemisorption on acidic surface interact with acidic protons, electron acceptor sites and hydrogen from neutral or weakly acidic hydroxyl groups. IR spectroscopy has been found to be a useful tool<sup>10-13</sup> in the determination of the nature of interactions between adsorbed bases and the acid sites on the surfaces of solids. In the present work the IR technique, has been used to identify the different types of acidic sites available on the surface of zirconium pillared clays using pyridine and ammonia as the probe molecules.

## Experimental

Zirconium pillared montmorillonite and vermiculite clay catalysts were prepared by suspension of sodium form of the clays in 1:1 acetone-water medium followed by the addition of zirconium oxychloride solution (0.05 - 0.15 M) dropwise with constant stirring. The mixture was aged at room temperature for 2 h. The solid was then filtered, washed and dried overnight at 100-110°C. It was calcined at 400°C for 16 h. The samples intercalated with 0.05, 0.1 and 0.15 M zirconium oxychloride solution are denoted as M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> for montmorillonite and V<sub>1</sub>, V<sub>2</sub>, V<sub>3</sub> for vermiculite. Chemical compositions of the zirconium pillared samples were determined by wet chemical analysis.

The adsorption of pyridine and ammonia was carried out on modified clay samples. The samples were degassed at  $1 \times 10^{-3}$  torr at 150°C and cooled to room temperature *in vacuo*. The bases were adsorbed by allowing their vapours to come into contact with the degassed samples. Excess of unadsorbed vapours and the bases physisorbed on the samples were removed by evacuation at  $1 \times 10^{-3}$  torr for several hours. IR spectra of raw and pillared clay samples were recorded on a Perkin-Elmer 983G spectrophotometer using KBr mull technique. The IR spectra of pyridine and ammonia adsorbed samples were recorded using self-supporting wafers of about 10-12 mg.

## Results and discussion

The IR adsorption spectra of raw montmorillonite and vermiculite show two characteristic regions, viz, the 3750-3500 cm<sup>-1</sup> region, which is characteristic of the surface hydroxyl groups and the 1150-400 cm<sup>-1</sup> region which is characteristic of lattice vibrations. The IR spectra of zirconium pillared montmorillonite and vermiculite samples showed the presence of a doublet in the O-H stretching region indicating the existence of two types of hydroxyl groups, viz, (i) a band at 3655 cm<sup>-1</sup> due to the lattice OH (ii) a band at 3700 cm<sup>-1</sup> due to the OH groups associated with the pillars. The adsorption bands in the region 1150-400 cm<sup>-1</sup> assigned to original clay structure remained unaltered on intercalation.

Pyridine, being a weaker base than ammonia, is considered to be a much more selective indicator for surface acidity<sup>14</sup>. Pyridine can interact with Lewis

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Table 1-Infrared(IR) absorption frequencies of ring vibrations of pyridine

Mode	IR frequencies( $\text{cm}^{-1}$ )			
	Liquid	HPY	LPY	BPY
19b	1439	1445-1440	1460-1445	1550-1530
19a	1478	1490-1480	1490-1478	1490-1478
8b	1572	1577	1585-1575	1613-1600
8a	1579	1600-1580	1632-1602	1640-1631

HPY - Hydrogen bonded pyridine  
 LPY - Pyridine adsorbed on lewis acid sites  
 BPY - Pyridine adsorbed on Brönsted acid sites

Table 2 -Infrared(IR) absorption frequencies of pyridine adsorbed on zirconium pillared clay catalyts

Observed IR frequencies ( $\text{cm}^{-1}$ )	Mode	Assignment indicating the type of acid site
Montmorillonite based catalyts		
1445-1430	19b	HPY+LPY
1491-1487	19a	HPY+LPY+BPY
1550-1539	19b	BPY
1600	8b	BPY
1642-1630	8a	LPY+BPY
Vermiculite based catalyts		
1450	19b	HPY+LPY
1480-1460	19a	HPY+LPY+BPY
1555-1545	19b	BPY
1600-1590	8b	BPY

acid sites to form a co-ordination complex or with acidic protons (Brönsted acid sites) to form pyridinium ion. The expected infrared frequencies of pyridine adsorbed on different acid sites are given in Table 1. The IR data of pyridine adsorbed on zirconium pillared montmorillonite ( $M_1$ ) are given in Table 2. The strong absorption band occurring at  $1445\text{-}1430\text{ cm}^{-1}$  has been assigned to 19b mode indicative of the presence of pyridine adsorbed on lewis acid sites as well as hydrogen bonded/physisorbed pyridine. The strong and sharp band in the region  $1491\text{-}1487\text{ cm}^{-1}$  has been assigned to 19a mode and is indicative of the presence of pyridine adsorbed on lewis acid sites, Brönsted acid sites as well as physisorbed pyridine. The broad band at  $1550\text{-}1539\text{ cm}^{-1}$  and the shoulder at  $1600$  and  $1590\text{ cm}^{-1}$

Table 3-Infrared (IR) absorption frequencies of ammonia adsorbed on zirconium pillared clay catalyts

Zirconium pillared clay catalyts	Observed IR frequencies for	
	Lewis acid site ( $\text{cm}^{-1}$ )	Brönsted acid site ( $\text{cm}^{-1}$ )
Montmorillonite-based	1672-1642	1468-1445
Vermiculite-based	1650-1648	1450-1439

have been assigned to the 19b and 8b modes respectively and indicate the presence of pyridine adsorbed on Brönsted acid sites. The multiplets at  $1640\text{-}1629\text{ cm}^{-1}$  have been assigned to the 8a mode and are indicative of pyridine adsorption on lewis acid sites as well as Brönsted acid sites. An overlap of the vibrations of pyridine occurs in this region indicating the presence of all three types of acidic sites on zirconium pillared montmorillonite catalyts. It is clear from the IR spectral data that zirconium pillared vermiculite catalyts show all the three types of acid sites.

The presence of Brönsted acid sites and lewis acid sites has been confirmed by the IR absorption band exclusive to these sites. However, the presence of hydrogen bonded pyridine is indicated but not confirmed by the IR bands. In order to confirm the existence of hydrogen bonded pyridine on weak acid sites incapable of protonating pyridine, the IR spectra of zirconium pillared montmorillonite sample ( $M_1$ ) was recorded after evacuating to  $1 \times 10^{-3}$  torr at room temperature,  $150^\circ\text{C}$  and  $250^\circ\text{C}$  respectively. It has been found that the intensity of the  $1455\text{ cm}^{-1}$  band decreases considerably after evacuating the pyridine adsorbed sample at  $150^\circ\text{C}$  but is not eliminated totally. This clearly indicates the adsorption of pyridine on lewis acidic sites and the desorption of hydrogen bonded pyridine from the surface, on heat-

ing the sample to 150°C. Evacuating the sample at 250°C totally desorbs the hydrogen bonded pyridine and also affects the intensities of 1445 and 1549  $\text{cm}^{-1}$  bands assigned to LPY and BPY.

Ammonia, being the smallest among the bases, easily penetrates the outer surface to be adsorbed even on inaccessible acidic sites besides moderately weaker acidic sites. Adsorption of ammonia occurs on Brönsted acidic sites due to the interaction of the nitrogen lone-pair electrons with the surface hydroxyl groups forming ammonium ion. Ammonia interacts with lewis acid site, through coordination. The IR data for the ammonia adsorbed zirconium pillared montmorillonite ( $M_1$ ) and vermiculite ( $V_1$ ) samples are given in Table 3. In the case of zirconium pillared montmorillonite samples two adsorption bands have been observed in the regions 1468-1445  $\text{cm}^{-1}$  and 1672-1642  $\text{cm}^{-1}$ . The band in the region 1672-1642  $\text{cm}^{-1}$  has been attributed to the bending vibration of ammonia co-ordinately linked to a lewis center. The adsorption band in the region 1468-1445  $\text{cm}^{-1}$  has been assigned to the characteristic vibration of the  $\text{NH}_4^+$  ion, indicating the presence of Brönsted acidic sites. It is clear from IR spectral data that zirconium pillared vermiculite has both lewis and Brönsted acid sites.

It can be concluded that intercalation of montmorillonite and vermiculite with polyoxo cationic species of zirconium enhances the acidity of the clays. The existence of different types of acid sites is revealed by the IR spectral studies on base adsorbed pillared clay catalysts. The presence of weak,

lewis and Brönsted acid sites on the catalyst surface is confirmed.

#### Acknowledgement

The authors thank the Department of Science and Technology, Government of India for providing financial assistance during the period of the work.

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