Infrared Spectroscopic Study of the Occupation of Hydrogen Cyanide Receptor Sites of Metallo-Oxide Pillared Clays by Hydrocarbons

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The decrease in the numbers of receptor sites for hydrogen cyanide on metallo-oxide pillared clays detectable by infrared spectroscopy, which occur when there is an initial exposure of the pillared clays to the various hydrocarbons, has been interpreted to be Lewis acid sites on the oxidic pillar material and Brønsted acid sites on the clay sheet along with a distinctive site resulting essentially from the pillar fixation process and have been used to define the reactivity of these receptor sites toward the hydrocarbons. 1-Hexene is an effective competitor for all the hydrogen cyanide receptor sites. The distinctive sites associated with the pillaring process while not exhibiting any marked selectivity toward the hydrocarbons, *n*-hexane, cyclohexane, benzene and toluene are most affected by the nature of the oxide pillar in the order Al > Cr > Ti > Zr > Fe. A measure of selectivity toward the hydrocarbons is shown by zirconium oxide pillared hectorite whose distinctive sites are more effectively tenanted by benzene or toluene than by *n*-hexane or cyclohexane.

Introduction

The reactive sites involved in the uptake of hydrogen cyanide by zeolites[1–3] and metallo-oxide pillared clays[4] have been characterized by FTIR spectroscopy. In the case of the pillared clays, the uptake of hydrogen cyanide arises from its binding to thermally generated Lewis acid sites on the metallo-oxidic pillar material, Brønsted acid sites associated with the clay sheet structure, and Brønsted acid sites formed upon cross-linking of pillar material to the clay sheets.[4] With this array of different binding sites for hydrogen cyanide, are they equally accessible or reactive toward other reactants particularly those involved in catalytic processes? To answer this question, the heat-treated pillared clays have been initially exposed to atmospheres of various hydrocarbons and subsequently allowed to take up hydrogen cyanide, the whole process being monitored by IR measurements. Comparisons with the uptake of hydrogen cyanide by pillared clays without prior treatment with hydrocarbons reveals selectivity of receptor sites. The present study deals with such procedures for variations of the oxidic pillar, clay type, and hydrocarbon. The IR measurements are based on the wavenumber shifts and increases in intensity of the ν_1 band of hydrogen cyanide from the free gas value which occur on its hydrogen bonding to Brønsted acid sites on the clay sheets or coordination by Lewis acid sites on the oxidic pillar material.

Experimental Section

The methodology of the preparation and characterization of metallo-oxide pillared clays, their fabrication into self-supporting wafers, heat treatment, exposure to hydrogen cyanide, and recording of the IR spectra due to adsorbed hydrogen cyanide has been explained previously.[4]

After initial treatment at diminished pressure, wafers of the pillared clays were mounted in the isolatable cell and they were exposed (1 h) to atmospheres of freshly distilled hydrocarbons, with removal of the excess hydrocarbon by a short period of pumping. The IR spectrum due to a particular hydrocarbon adsorbed by the wafer was recorded. The wafer was then exposed to hydrogen cyanide and the IR spectrum due to the adsorbed hydrogen cyanide was recorded.

The amount of each hydrocarbon adsorbed on each pillared clay was determined by the mass increases which occurred after exposure of the preheated (673 K for 1 h) pillared clay to an atmosphere of hydrocarbon at 293 K for 3 h.

Results

A previous study[4] has shown that the population of hydrogen cyanide receptor sites associated with the oxide pillar material increases with temperature over the range 473–673 K, while uptake by sites on the clay sheet material decreases over this temperature range. To obtain maximum sensitivity of the clay sheet sites the lower temperature range was used for initial thermal treatment of the pillared clay while thermal treatment at 603 K was a compromise temperature for ease of observation of both types of hydrogen cyanide adsorption.

Infrared spectral measurements were made on selected hydrocarbon treated oxide pillared montmorillonite samples initially heated to 673 K. While possessing larger IR spectral band intensities due to the subsequent adsorption of hydrogen cyanide on Lewis acid sites (2220 cm^{-1}) and smaller IR spectral band intensities due to Brønsted acid sites (2148, 2099 cm^{-1}), the percentage differences in spectral intensities between the hydrocarbon-treated and -untreated clays were closely similar to those obtained at the lower initial temperature (603 K) of thermal treatment of the pillared material.

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1995.

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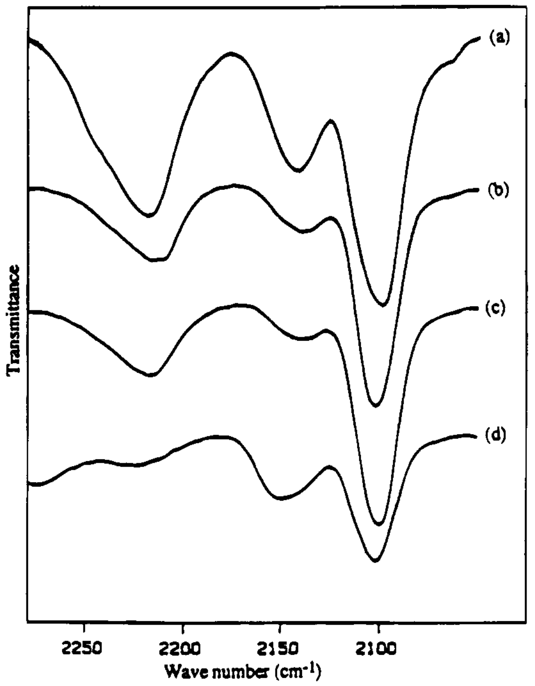

Figure 1. (a) IR spectra due to hydrogen cyanide adsorbed by aluminum oxide pillared montmorillonite initially heated to 603 K and exposed to an atmosphere of (b) *n*-hexane, (c) benzene, and (d) 1-hexene.

Table 1. Decreases in IR Spectral Band Areas Due to Hydrogen Cyanide Adsorbed on Hydrocarbon-Treated (1) Aluminum Oxide Pillared Montmorillonite and (2) Zirconium/Aluminum Oxide Pillared Montmorillonite Initially Heated to 603 K

pillared montmorillonite	IR spectral band areas (cm^{-1} mg^{-1}) centered in the region 2220 cm^{-1}	2148 cm^{-1}	2099 cm^{-1}
1. Aluminum Oxide			
(a) before hydrocarbon treatment	0.51	0.16	0.64
after adsorption of			
(b) *n*-hexane	0.16	0.04	0.35
(c) benzene	0.15	0.03	0.33
(d) 1-hexene	0.00	0.07	0.14
2. Zirconium/Aluminum Oxide			
(a) before hydrocarbon treatment	0.60	0.16	0.76
after adsorption of			
(b) *n*-hexane	0.21	0.06	0.37
(c) benzene	0.09	0.03	0.40
(d) 1-hexene	0.00	0.06	0.09

Figure 1 shows the influence of treatment of wafers of aluminum oxide pillared montmorillonite, initially heated to 603 K with *n*-hexane, benzene, and 1-hexene on the IR spectra due to hydrogen cyanide adsorbed after hydrocarbon adsorption while the spectral band areas are outlined in Table 1. The IR spectral features due to the adsorbed hydrocarbons with respect to wavenumber and band intensity are unaffected by the hydrogen cyanide. Largely similar results were obtained for adsorption of hydrogen cyanide on hydrocarbon-treated titanium, zirconium, iron, and chromium oxide pillared clays. The reductions in the areas of the IR spectral bands due to adsorbed hydrogen cyanide by the various hydrocarbon-treated oxide pillared montmorillonites are summarized in Table 2.

Table 2. Comparisons of IR Spectral Band Areas Due to Hydrogen Cyanide Adsorbed by Hydrocarbon-Treated Oxide-Pillared Montmorillonites Initially Heated to 473 K with Those of the Untreated Pillared Montmorillonites

pillared montmorillonite	IR spectral band areas (cm^{-1} mg^{-1}) centered in the region 2099 cm^{-1}	2148 cm^{-1}
1. Aluminum Oxide		
(a) before hydrocarbon treamtent	0.86	0.18
after adsorption of		
(b) *n*-hexane	0.57	0.02
(c) cyclohexane	0.59	0.03
(d) benzene	0.56	0.01
(e) toluene	0.57	0.01
2. Zirconium Oxide		
(a) before hydrocarbon treatment	0.54	0.28
after adsorption of		
(b) *n*-hexane	0.35	0.17
(c) cyclohexane	0.35	0.15
(d) benzene	0.28	0.14
(e) toluene	0.35	0.18
3. Titanium Oxide		
(a) before hydrocarbon treatment	0.78	0.30
after adsorption of		
(b) *n*-hexane	0.49	0.14
(c) cyclohexane	0.45	0.12
(d) benzene	0.31	0.12
(e) toluene	0.43	0.11
4. Iron Oxide		
(a) before hydrocarbon treatment	0.79	0.22
after adsorption of		
(b) *n*-hexane	0.42	0.12
(c) cyclohexane	0.40	0.14
(d) benzene	0.39	0.13
(e) toluene	0.40	0.15
5. Chromium (Aged) Oxide		
(a) before hydrocarbon treatment	0.89	0.31
after adsorption of		
(b) *n*-hexane	0.56	0.05
(b) cyclohexane	0.54	0.07
(c) benzene	0.44	0.04
(d) toluene	0.51	0.09

The effects of initial adsorption of various hydrocarbons on the IR spectral bands due to subsequently adsorbed hydrogen cyanide by zirconium/aluminum mixed oxide pillared montmorillonite heated to 603 K are shown by Figure 2, while the spectral band areas are summarized by Table 1. The diminished areas of the IR spectral bands due to adsorbed hydrogen cyanide on mixed oxide pillared montmorillonite initially heated to 473 K and exposed to atmospheres of various hydrocarbons are summarized in Table 3.

The reductions in IR spectral band intensities due to hydrogen cyanide adsorbed by aluminum oxide pillared hectorite and zirconium oxide pillared hectorite initially heated to 603 K which occur as a result of prior adsorption of various hydrocarbons are shown by Figures 3 and 4, respectively, while the corresponding decrease in IR spectral band areas are summarized in Table 4. The decreases in the IR spectral band areas due to hydrogen cyanide which occur as a result of initial hydrocarbon adsorption on both aluminum and zirconium oxide pillared hectorite first heated to 473 K are summarized in Table 5.

To gain information on the amounts of hydrocarbons taken up by the various pillared clays, they were first heated to 673 K for maximal generation of Lewis acid sites and exposed to atmospheres of the various hydrocarbons. The amounts of each hydrocarbon adsorbed was determined gravimetrically. The results are summarized by Table 6.

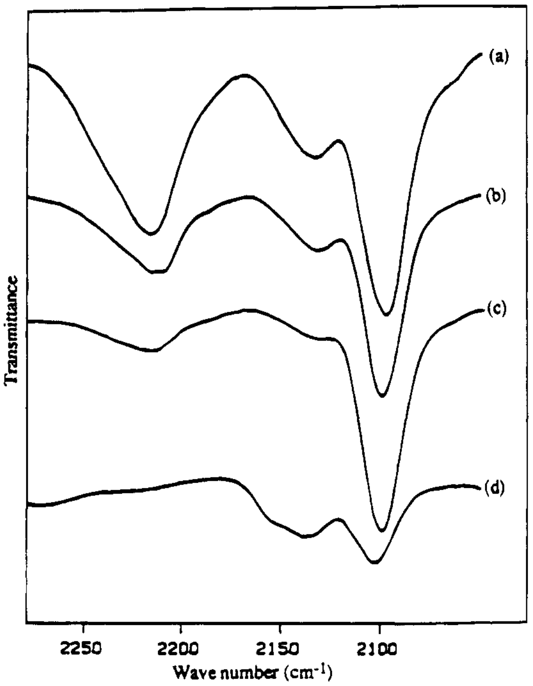

Figure 2. (a) IR spectra due to hydrogen cyanide adsorbed by zirconium/aluminum oxide montmorillonite initially heated to 603 K and exposed to an atmosphere of (b) *n*-hexane, (c) benzene, and (d) 1-hexene.

Table 3. Comparisons of IR Spectral Band Areas Due to Hydrogen Cyanide Adsorbed by Hydrocarbon-Treated Mixed Oxide Pillared Montmorillonites Initially Heated to 473 K with Those of the Untreated Pillared Montmorillonites

mixed oxide pillared montmorillonite	IR spectral band areas (cm^{-1} mg^{-1}) centered in the region	
	2099 cm^{-1}	2148 cm^{-1}
1. Aluminum/Zirconium		
(a) before hydrocarbon treatment	0.91	0.28
after adsorption of		
(b) *n*-hexane	0.51	0.08
(c) cyclohexane	0.66	0.10
(d) benzene	0.44	0.08
(e) toluene	0.44	0.07
2. Chromium/Zirconium		
(a) before hydrocarbon treatment	1.05	0.25
after adsorption of		
(b) *n*-hexane	0.55	0.13
(c) cyclohexane	0.57	0.08
(d) benzene	0.51	0.07
(e) toluene	0.54	0.11
3. Iron/Zirconium		
(a) before hydrocarbon treatment	1.17	0.32
after adsorption of		
(b) *n*-hexane	0.70	0.06
(c) cyclohexane	0.72	0.07
(d) benzene	0.05	0.03
(e) toluene	0.65	0.08

Discussion

Among the hydrocarbons, 1-hexene exerts the greatest influence in reducing the number of receptor sites potentially available to hydrogen cyanide giving a clear indication that both hydrogen cyanide and alkene interact with the same Brønsted and Lewis acid sites. Indeed, the indiscriminate reaction of 1-hexene with all the acid sites detracts from its use to discern any measure of selectivity of interaction. The interaction of the hydrocarbons with the Lewis acidity generated at the higher temperatures of initial heat treatment of aluminum oxide, zirconium/aluminum oxide pillared montmorillonite, and aluminum oxide or zirconium oxide pillared hectorite increases in the order 1-hexene > benzene > *n*-hexane with some selectivity, shown in Tables 1 and 4, toward benzene by the Lewis acidity developed by the zirconium oxide pillar material in hectorite or zirconium/aluminum oxide pillar material in montmorillonite where the percentage of Lewis acid

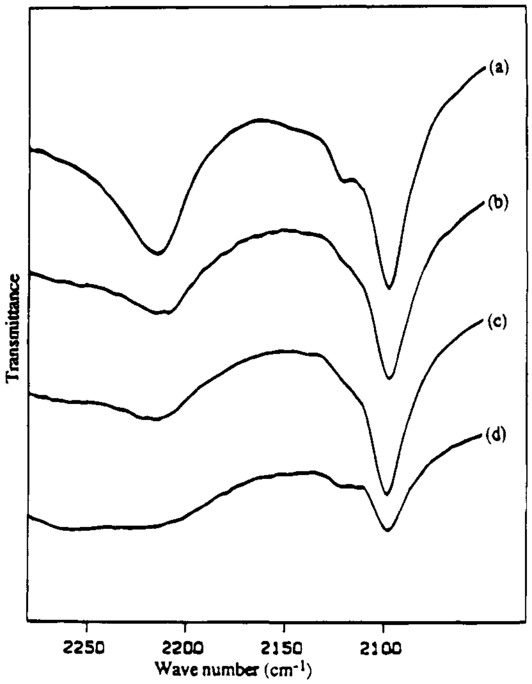

Figure 3. (a) IR spectra due to hydrogen cyanide adsorbed by aluminum oxide pillared hectorite initially heated to 603 K and exposed to an atmosphere of (b) *n*-hexane, (c) benzene, and (d) 1-hexene.

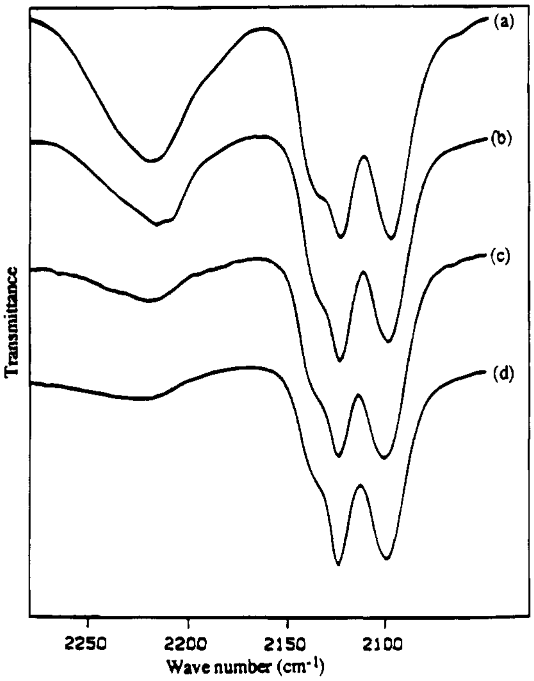

Figure 4. (a) IR spectra due to hydrogen cyanide adsorbed by zirconium oxide pillared hectorite initially heated to 603 K and exposed to an atmosphere of (b) *n*-hexane, (c) benzene, and (d) 1-hexene.

Table 4. Decreases in IR Spectral Band Areas Due to Hydrogen Cyanide Adsorbed by Hydrocarbon-Treated (1) Aluminum Oxide Pillared Hectorite and (2) Zirconium Oxide Pillared Hectorite Initially Heated to 603 K

	IR spectral band areas (cm^{-1} mg^{-1}) centered in the region		
pillared hectorite	2220 cm^{-1}	2148 cm^{-1}	2099 cm^{-1}
1. Aluminum Oxide			
(a) Before hydrocarbon treatment	0.51	0.10	0.38
after adsorption of			
(b) *n*-hexane	0.24	0.00	0.34
(c) benzene	0.21	0.00	0.31
(d) 1-hexene	0.00	0.03	0.09
2. Zirconium Oxide			
(a) before hydrocarbon treatment	0.49	0.64	0.48
after adsorption of			
(b) *n*-hexane	0.23	0.28	0.32
(c) benzene	0.08	0.37	0.29
(d) 1-hexene	0.05	0.28	0.25

sites available to hydrogen cyanide is remarkably similar.

The reductions in the IR spectral band areas in the 2099 cm^{-1} region due to adsorption of hydrogen cyanide on hydrocarbon treated metallo-oxide pillared montmorillonite, as indicated by Table 2, are not greatly affected by the nature of the hydrocarbon or the metallo-oxide used for the pillaring process. In contrast, the decreases in IR spectral band areas in the region of 2148 cm^{-1}, which represents receptor sites specifically associated with the pillaring process, while not exhibiting a discernible selectivity toward the hydrocarbons listed in Table 2 show a marked dependence on the nature of the oxide pillar with the greatest losses in IR spectral areas occurring in the order Al > Cr > Ti > Zr > Fe. The effect of the hydrocarbons on the subsequent adsorption of hydrogen cyanide by aluminum oxide pillared hectorite, as indicated by Table 5, is not greatly different from that of the pillared montmorillonite while zirconium oxide pillared hectorite shows some selectivity in its interaction with aromatic hydrocarbons at its sites represented by the 2148 cm^{-1} band.

Table 5. Decreases in IR Spectral Band Areas Due to Hydrogen Cyanide Adsorbed by Hydrocarbon-Treated (1) Aluminum Oxide Pillared Hectorite and (2) Zirconium Oxide Pillared Hectorite Initially Heated to 473 K

	IR spectral band areas (cm^{-1} mg^{-1}) centered in the region	
pillared hectorite	2099 cm^{-1}	2148 cm^{-1}
1. Aluminum Oxide		
(a) before hydrocarbon treatment	0.61	0.13
after adsorption of		
(b) *n*-hexane	0.39	0.03
(c) cyclohexane	0.40	0.08
(d) benzene	0.26	0.02
(e) toluene	0.33	0.3
2. Zirconium Oxide		
(a) before hydrocarbon treatment	0.92	0.89
after adsorption of		
(b) *n*-hexane	0.56	0.61
(c) cyclohexane	0.54	0.75
(d) benzene	0.55	0.37
(e) toluene	0.58	0.42

Table 6. Amount of Hydorcarbon Adsorbed by the Thermally Treated (673 K) Pillared Clays at 293 K, Expressed as mmol of Hydrocarbon/g of Clay

	amount of hydrocarbon adsorbed (mmol g^{-1})			
oxide pillared clay	*n*-hexane	cyclohexane	benzene	1-hexene
Al montmorillonite	0.905	0.974	1.55	1.45
Zr montmorillonite	1.02	0.939	1.65	1.58
Ti montmorillonite	1.07	1.06	1.64	1.83
Fe montmorillonite	1.01	1.02	1.60	1.79
Cr montmorillonite	0.970	0.983	1.43	1.48
Al/Zr montmorillonite	1.13	1.18	1.61	1.62
Cr/Zr montmorillonite	1.15	1.21	1.68	1.68
Fe/Zr montmorillonite	1.09	1.10	1.59	1.63
Al hectorite	0.719	0.701	0.819	0.915
Zr hectorite	0.756	0.748	0.832	0.927

In their potential use as catalysts in hydrocarbon processing, among the pillared clays, aluminum oxide pillared montmorillonite offers the best range of acidic receptor sites, with more than two-thirds of its Lewis acid sites, one-third of its clay-sheet sites, and nearly all of its distinctive sites formed in the pillaring process available to hydrocarbons. The beneficial effect of the binding of hydrocarbons by aluminum oxide in the pillar material as indicated by Table 3 persist in the mixed oxide pillared montmorillonite.

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