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Montmorillonite Clay Catalysis: Conversion of Methyl Benzoate and NH_3 into Benzonitrile and Amides[1]

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The reaction of methyl benzoate [1] with NH_3 was studied over Montmorillonite K10 clay in the temperature range 280–340°C. Benzonitrile [2], benzoic acid [3], benzamide [4], N-methylbenzamide [5], and methanol were formed as products in varying amounts. This reaction was investigated as a function of molar ratio of 1 to NH_3, temperature, and contact time. At $1/NH_3 = 0.5$, 320°C, and contact time of 1.96×10^{-3} h the conversion of 1 was 64.7% and the selectivities of 2 and 4 + 5 were 59.6 and 20.2, respectively. The clay catalyst was equally active for other aromatic and aliphatic esters. At 340°C and 67.2% conversion of ethyl propionate the selectivity to propionitrile was 73.3 after 4 h reaction. The actual pathways leading to formation of products was studied in detail. ESCA, NH_3 adsorption, pyridine adsorption, and IR studies, in combination with the catalytic investigation show that NH_3 adsorbed on the acidic >Al–OH sites forms ammonium ions [NH_4^+] which participate in the reaction. The Lewis acid sites are likely to be involved in the formation of 2. The clay catalyst undergoes deactivation on continuous use for several hours [23 h]. The deactivation is mainly due to dealumination by water produced in the reaction and accumulation of organic residue containing an amide group on the surface of the clay. It was also possible to calculate effective active sites on the catalyst surface and then a correlation with the turnover of formation of benzonitrile could be established.

1. INTRODUCTION

Synthesis of nitriles is an important catalytic and industrial process (1–3). They are increasingly being used in selective solvent extraction, as reaction media, as intermediates in preparation of pharmaceuticals (4) and a variety of commercial amines and amides, as jet-fuel additives, in cotton bleaching baths, etc. The nitriles are produced in high yield by vapour-phase catalytic ammoxidation of olefins (5), alkanes (6), and aromatics (7) using multimetal-containing oxides.

Dehydration of carboxamides to nitriles is also known using dehydrating agents (8) like PCl_5, $SOCl_2$, acid anhydrides, and catalysts like $AlCl_3$ and $ZnCl_2$ (9). Preparation of benzonitrile by the catalytic reaction of toluene with NO has been reported (10). A method for making benzonitrile by dehydrogenation of the Diels–Alder adduct of butadiene and acrylonitrile is also available (11). Reaction of ethanol and NH_3 to give acetonitrile over SAPO (40 type) and V–Y zeolites is recently reported (12). It has also been shown that nitriles can be prepared from carboxylic acids and NH_3 over silica gel (13), ThO_2, Al_2O_3, and zeolite catalysts (14). Application of this reaction is industrially significant only when carboxylic acids are cheaper and more accessible than their nitrile (3).

In the petrochemicals industry conversion of C_8 cut to dimethyl terephthalate (DMT) produces a sizeable quantity of methyl benzoate as by-product. Conversion of this ester into benzonitrile with NH_3 is an attractive proposition.

Synthesis of organic compounds employing environmentally benign Montmorillonite clay catalyst is an area of our current interest (15–17). In this study conversion of methyl benzoate and other esters to nitriles has been carried out with NH_3 on Montmorillonite clay catalyst. Identification of acid sites involved in the reaction, recycle of the catalyst, and a possible deactivation pathway of the clay catalyst have been studied using ESCA and NH_3 adsorption.

2. EXPERIMENTAL

2.1. Materials

Montmorillonite K10 clay was purchased from Fluka AG, Switzerland. It has the weight-percent composition of $SiO_2 = 70$, $Al_2O_3 = 15$, $Fe_2O_3 = 1.5$, $CaO = 2.5$, $MgO = 3$, $Na_2O = 0.5$, $K_2O = 1.5$, and $H_2O = 6$. It has bulk density = 300 ± 30 g/l and surface area = 200 ± 10 m^2/g. Na^+-Montmorillonite was prepared from K10 clay by ion exchange method (18). Nb_2O_5 was purchased from Loba Chemicals, Bombay. Methyl benzoate (94% pure) and methyl p-toluate of IPCL, Baroda were used. Ethyl benzoate was supplied by High purity chemicals, New Delhi. Ethyl propionate and ethyl phenylacetate were prepared from the corresponding acids and ethanol by extractive esterification (19). Ammonia [99.8% purity] supplied in

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cylinder by GSFC, Baroda was used as such. The HZSM-5 sample was synthesized by hydrothermal crystallization method and characterized (20). HY zeolite was synthesized from NaY zeolite (IPCL, Baroda) by NH_4^+ exchange followed by calcination at 550°C. The final HY zeolite has a frame work Si/Al of 3.

The powder form of the catalyst material was converted into extrudates of 1.5 mm diameter by 2–3 mm length (predominantly 3 mm long) and then calcined at 250°C for 2 h. The selectivity to amide formation is independent of the size of the extrudates. On the other hand, the selectivity to benzonitrile is maximum in the size of the extrudates used (2–3 mm).

2.2. *Reaction Procedure*

The reaction was carried out in a tubular, down-flow reactor (20 mm ID); 2 g of Montmorillonite K10 was loaded into the reactor. The temperature was set at 320°C. Distilled methyl benzoate was fed (3 ml/h; 0.0234 mol/h) from the top using a Sage Syringe pump. Equimolar quantity of NH_3 (600 ml/h; 0.0234 mol/h), measured through a gas flow meter and N_2 gas (1200 ml/h) were flown on the catalyst bed. The product mixture coming out of the reactor was condensed by circulating chilled water (5°C). Samples were collected at 1 h intervals. The products were characterised by GC-MS (HP 5890) and ^{1}H NMR (Jeol JNM FX100). The course of the reaction was monitored by GC using 2 m 1.5% OV-17 column in a Shimadzu 15A GC fitted with flame ionization detector. The conversion and selectivity were determined in the following way:

$$\text{Conversion of methyl benzoate (mol\%)} = \frac{\text{Moles of converted methyl benzoate} \times 100}{\text{Moles of methyl benzoate fed}}$$

$$\text{Selectivity to benzonitrile (mol\%)} = \frac{\text{Moles of benzonitrile formed} \times 100}{\text{Moles of converted methyl benzoate}}$$

$$\text{Converted methyl benzoate} = \text{methyl benzoate fed} - \text{unreactedmethyl benzoate collected.}$$

$$\text{Turnover number (TON) of } \mathbf{2} = \frac{\text{Moles of } \mathbf{2} \text{ formed}}{\text{Estimated Lewis acid sites on the catalyst}}$$

$$\text{Turnover number (TON) of } (\mathbf{4}+\mathbf{5}) = \frac{\text{Moles of } (\mathbf{4}+\mathbf{5}) \text{ formed}}{\text{Estimated total Brønsted \& Lewis acid sites on the catalyst}}$$

$$\text{Turnover frequency (TOF)} = \text{TON/Time (s).}$$

C, H, and N analyses were carried out using the Elemental analyser (Carlo Erba, EA-1106).

2.3. *Acidity Measurement*

The acidity of the clay catalyst was determined independently by means of NH_3 and pyridine adsorption. A known weight (0.1 g) of the sample was placed in a microreactor (Catalytic Data System, Baroda) and heated at 250°C for 1 h. Known pulses (0.5 ml) of NH_3/pyridine (1 μl) were flown onto the clay sample along with the diluant He gas. The unadsorbed NH_3 or pyridine was estimated by thermal conductivity detector. Difference between the fed and unabsorbed NH_3 or pyridine gives the acidic sites on which NH_3 or pyridine are adsorbed. Pyridine adsorptions were carried out in the temperature range 280–340°C.

2.4. *IR Measurements*

Infrared spectra were recorded on Nicolet-550 FT-IR spectrometer equipped with OMNIC Nicolet FTIR software.

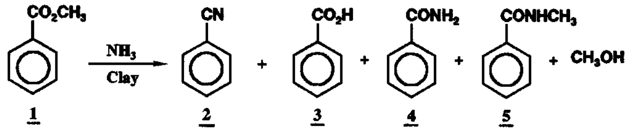
1 g of Montmorillonite K10 clay was activated in the temperature range 280–340°C and its IR spectrum was recorded (A). This sample was then treated with 1.5 ml of pyridine for 2 h. Then the excess base was removed under vacuum for 5 h and the pyridine adsorbed IR spectrum (B) was recorded. The concentrations of Brønsted and Lewis sites were calculated after substracting spectrum A from B.

2.5. *ESCA Measurements*

A Vacuum Generators ESCALAB MK II spectrometer with a MgK$_\alpha$ radiation source (1253.6 eV) was used for the recording of XPS spectra. The anode was operated at 10 kV and 10 mA and the vacuum in the analysis chamber was maintained at better than 5×10^{-8} m bar. The spectrometer was calibrated using Cu ($2p_{3/2}$) and Ag ($3d_{5/2}$) photoelectron lines at 932.7 and 368.3 eV, respectively (21, 22). Samples were placed onto double side adhesive tape and mounted on sample holders. These samples were kept overnight in the preparation chamber before they were transferred to the analysis chamber of the spectrometer for analysis. The Si ($2p$) photoelectron line at 103.0 eV was used as an internal reference (23–25) for the correction of the charging effect. Data were collected and analysed on Apple IIe computer interfacing the spectrometer.

3. RESULTS AND DISCUSSION

The reaction of methyl benzoate [**1**] with NH_3 over Montmorillonite K10 gave benzonitrile [**2**], benzoic acid [**3**], benzamide [**4**], N-methylbenzamide [**5**], and methanol as products



in varying amounts. The reaction was run on the extruded form of clay catalyst as the flow of reactants was smoother through such a catalyst bed than through the powder form of catalyst. Further, it is observed that Si/Al of 4.27 in the powder clay surface is changed to 3.15 in the extrudates. This has a beneficial effect on the reaction.

3.1. *Effect of Reaction Time*

On fresh Montmorillonite K10 catalyst the conversion of methyl benzoate is high and the activity slowly decreases with the increase in time on stream. Figure 1 shows the typical selectivity and turnover frequencies (TOF) for benzonitrile [**2**] and the amides [**4**, **5**].

3.2. *Effect of Reaction Temperature*

Figure 2 shows the results of the reaction on Montmorillonite K10 in the temperature range 250–350°C in 6 h run. It was observed that the reaction was unsuccessful at temperatures below 250°C. The level of methyl benzoate conversion increased with increasing reaction temperature. Selectivity to benzonitrile slowly increases with temperature and after 320°C it remains constant. Formation of amides [**4**, **5**] remains steady throughout the temperature range 280 to 340°C. TOFs of both **2** and **4** + **5** increase with the increase in temperature. However, nitrile formation is higher at 340°C relative to the amides. From the Arrhenius plot the apparent energy of activation ($E_a^{\#}$) of benzonitrile and the amide formation were calculated to be 11.3 and 9.4 kcal/mol, respectively. At 320°C and 63% conversion of methyl benzoate the selectivity to benzonitrile and amides are 48.1 and 24.1, respectively. For the subsequent study the reaction temperature was fixed at 320°C.

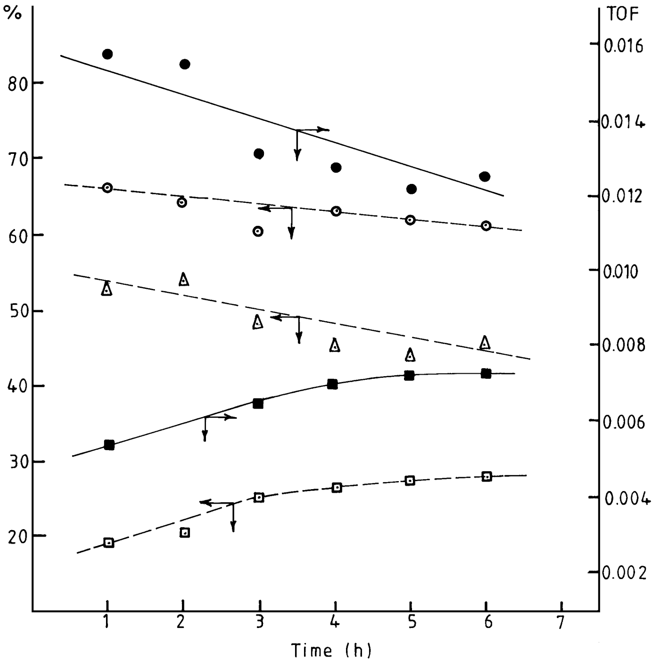


FIG. 1. Effect of reaction time: **1** : NH_3 = 1 : 1 (molar); 320°C; 2 g clay; N_2 = 20 ml/min. (⊙) Conversion of **1**; (△) selectivity to **2** (●); (⊡) selectivity to [**4** + **5**] (■).

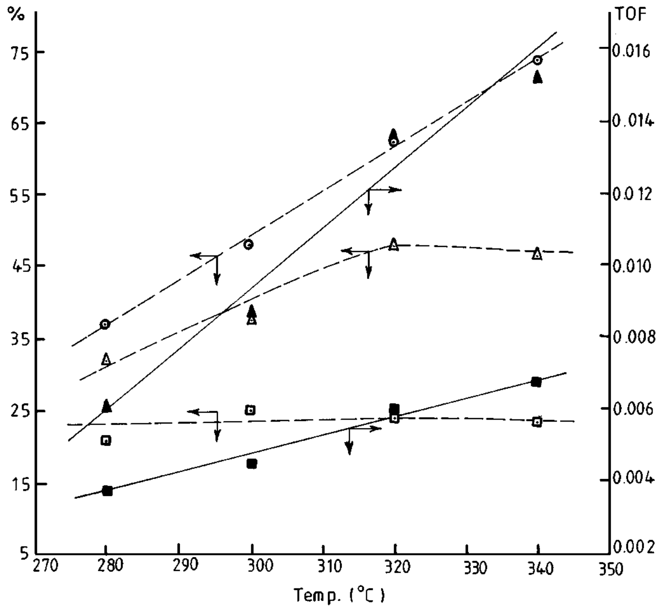


FIG. 2. Effect of reaction temperature: **1** : NH_3 = 1 : 1 (molar); N_2 = 20 ml; 2 g clay. (⊙) Conversion of **1**; (△) selectivity to **2** (▲); (⊡) selectivity to **4** + **5** (■).

3.3. *Reaction of Different Esters with Ammonia*

The activity of the clay catalyst was examined in the reaction of NH_3 with various esters (Table 2). Most of the esters gave the corresponding nitriles, amides, and alkylated amides. The amides were not obtained in the case of ethyl propionate. This is the case with ethyl acetate also as only acetonitrile was formed. This suggests that the conversion of the intermediate amide into nitrile is quite fast with aliphatic esters. Ethyl phenylacetate gave the highest selectivity to nitrile among the various esters tried.

3.4. *Reaction of Methyl Benzoate [1] and NH_3 over Various Catalysts*

The conversion of **1** (Table 1) and selectivity to **2**, **4**, and **5** over different catalysts are depicted in Table 1. All the catalysts were activated at the reaction temperature in a flow of N_2 for 2–3 h prior to startup of the reaction. The reactivity of Montmorillonite K10 in this reaction leading to the formation of **2**, **4**, and **5** is quite high. On the HZSM-5 catalyst, even though conversion of **1** is high, the selectivity to **2** is lower than on the clay catalyst. Na^+-Montmorillonite K10, as expected, offers low reactivity and selectivity to **2** and amides. The commercial ammoxidation catalyst has bare minimum activity for the formation of the nitrile. On Nb_2O_5

TABLE 1

Reaction of 1 and NH_3 over Different Catalysts[a]

Catalyst	Temp. (°C)	Time on stream (h)	Percent conv. of **1**	Selectivity to **2**	**(4 + 5)**
Montmorillonite K10	320	1	66.7	52.5	18
		6[b]	62.8	48.1	24.1
Na^+-Montmorillonite K10	320	6[b]	45.0	30.7	19.4
H-ZSM5	320	6[b]	60.4	22.4	28.8
Nb_2O_5	320	6[b]	23.8	12.0	—
Nb_2O_5	350	6[b]	23.5	14.0	—
Commercial ammoxidation catalyst	320	5[b]	39.0	3.0	—
H-Montmorillonite K10	320	1	72.6	50.7	7.1
		5[b]	69.1	33.2	19.4
γ-Al_2O_3	320	1	93.1	57.3	3.3
		5[b]	86.5	48.6	11.3

[a] Catalyst = 2 g; **1** : NH_3 = 1 : 1 (molar ratio); N_2 = 30 ml/min.
[b] Integral value.

interestingly, the amides are not formed, even though the selectivity to nitrile is poor. This difference can be attributed to the difference in the acidity of the catalysts.

3.5. *Effect of Molar Ratio of **1** to NH_3*

Various molar ratios of **1** to NH_3 were flown over the clay catalyst and the results are given in Table 3. Data collected over a 6 h period shows this ratio does not influence the overall conversion of **1**. Selectivity to **2** is high when the ratio of **1** to NH_3 has been 0.5. On the other hand, the selectivity to **4** and **5** is increased when **1**/$NH_3 > 1$. This suggests that at higher concentration of NH_3, MeOH, and H_2O formed in the reaction are quickly removed from the active sites, driving the reaction towards the formation of **2**.

TABLE 2

Reaction of Various Esters with NH_3 over Montmorillonite K10[a]

Ester	Time on stream	Percent conv. of ester	Selectivity to nitrile	amides
Methyl benzoate	6 h	62.8	48.1	24.1
	5 h	63.3	48.5	23.5
	4 h	63.6	49.7	22.6
Ethyl benzoate	6 h	34.2	50.0	20.1
	5 h	39.0	40.3	17.0
	4 h	37.2	38.0	15.0
Methyl p-toluate[b]	5h	51.6	38.9	23.4
	4 h	52.4	40.3	23.7
Ethyl phenylacetate	5 h	59.5	66.6	33.3
	4 h	60.5	67.2	32.8
Ethyl propionate	6 h	58.4	44.5	—
	5 h	57.4	46.1	—
	4 h	59.2	43.6	—
Ethyl propionate[c]	4 h	67.2	73.3	—

[a] Clay = 2 g; ester : NH_3 = 1 : 1 (molar ratio); 320°C; N_2 = 30 ml/min.
[b] Heptane is used as diluent.
[c] At 340°C.

TABLE 3

Effect of Molar Ratio of Methyl Benzoate to NH_3 (1/NH_3)[a]

No.	**1**/NH_3 (molar ratio)	Percent conv.[b] **1**	Selectivity[b] to **2**	**(4 + 5)**
1	1	62.8	48.1	24.1
2	0.5	64.7	59.6	20.2
3	>1	61.4	19.6	27.7
4	0.2	67.0	44.8	14.7

[a] Montmorillonite K10 2g; 320°C; N_2 = 30 ml/min.
[b] Average values of 6 h run.

3.6. *Effect of Contact Time*

The results (Table 4) show how the contact time affects the conversion of **1** and selectivity to the products. As expected both conversion of **1** and selectivity to all the products increase with the increase in contact time. However, the yield of product is less at the highest contact time, suggesting triggering off some other side reaction.

3.7. *Reaction Pathways*

In order to establish the actual pathways leading to the formation of products, various combinations of substrates, products, and catalyst were studied (Table 5). The products **2**, **3**, **4**, and **5** are formed only when methyl benzoate and NH_3 are reacted over the Montmorillonite K10 at elevated temperature. A one-to-one weight ratio of benzamide [**4**] and the clay was mixed and heated at 320°C in the flow reactor under a flow of N_2. The solid product recovered from the reactor after 2 h shows the formation of benzoic acid

TABLE 4

Effect of Contact Time[a]

No.	Contact time[b] (h)	Percent conv.[c] **1**	Selectivity[c] to (yield[d]) **2**	**(4 + 5)**
1	0.00598	79.5	45.7[0.0110]	18.7[0.0038]
2	0.00196	64.7	59.6[0.0285]	20.2[0.0097]
3	0.00098	52.4	49.7[0.0313]	13.9[0.0087]
4	0.00049	35.6	35.4[0.0363]	7.9[0.0081]

[a] 320°C; Montmorillonite K10; **1** : NH_3 = 1 : 2.
[b] Contact time = [Volume of clay catalyst × time]/[Volume of gas flown].
[c] Average values of 6 h run.
[d] Yield = moles of product formed per gram of catalyst in 5 h run.

TABLE 5

Reactivities of Substrates/Product on the Clay Catalyst

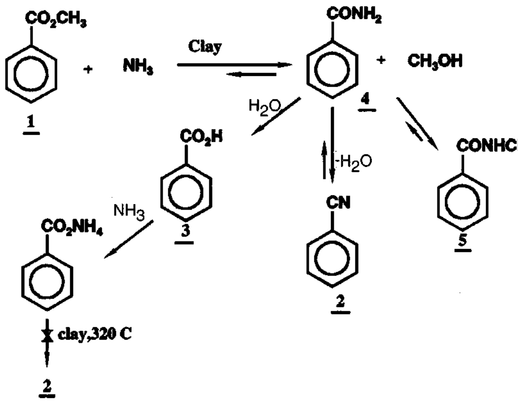
No.	Substrate[a]	Catalyst	Products
1	Methyl benzoate	—	—
2	Methyl benzoate	Montmorillonite K10	—
3	Methyl benzoate + NH_3	—	—
4	Methyl benzoate + NH_3	Montmorillonite K10[b]	**2**, **3**, **4**, **5**
5	Benzamide	Montmorillonite K10[b]	**3**
6	Propionic acid + NH_3	Montmorillonite K10	Ammonium propionate
7	Ammonium propionate	Montmorillonite K10[c]	—

[a] $N_2 = 30$ ml/min; 320°C.
[b] Catalyst = 2 g; **1** : NH_3 = 1 : 1 (molar ratio); $N_2 = 30$ ml/min; 320°C.
[c] Catalyst = 2 g; $N_2 = 30$ ml/min; 320°C.

[**3**]. The most probable reaction here is the interaction of **4** with water molecules trapped inside the layers of Montmorillonite clay. The benzoic acid formed in this reaction was reacted with NH_3 over clay at 320°C but part of it sublimed and choked the reactor. Hence, another acid, namely propionic acid, was allowed to react with NH_3 over the catalyst. Only ammonium propionate was formed at 320°C over the clay catalyst. In another run 10 wt% of methanol was fed, along with methyl benzoate [**1**] and NH_3, over Montmorillonite K10 and the selectivity of the products was compared with the selectivity of products from methyl benzoate [**1**] and NH_3 feed. On the addition of methanol, the selectivity to **4** and **2** is drastically reduced. When this feed was replaced by methyl benzoate [**1**] and NH_3 the selectivity to **4** and **2** increased. This clearly proves that the first step of the reaction of methyl benzoate and NH_3 involves the formation of benzamide [**4**] and methanol in an equilibrium reaction.

Similarly the influence of the mixtures of **1**, **4**, NH_3 and **1**, NH_3 feeds on Montmorillonite clay were compared. Here the addition of **4** suppresses the selectivity to **2** because, as in the case of the methanol addition run, the forward reaction of **1** and NH_3 leading to **4** and the methanol is suppressed. When the mixture comprising **1**, **4**, and NH_3 is replaced by **1** + NH_3 feed, the selectivity to **2** is not increased. This study suggests that both **1** and **4** compete for the same sites on the clay surface. As the NH_3 adsorbed on clay cannot react with **4**, as it does with **1**, the active sites are not regenerated. When benzamide [**4**] and methanol are heated at 190°C in the presence of the clay catalyst in an autoclave for about 2 h benzonitrile [**2**], N-methylbenzamide [**5**], and **1** are detected in the organic fraction. This further establishes that the formation of **4** from **1** is reversible in nature. However, the same mixture on heating at 140°C for 14 h does not give benzonitrile.

Based on the above study the reaction pathways involved in this reaction can be arrived as



Conversion of esters to amides and N-substituted amides and the dehydration of amide to nitrile are known to be acid catalyzed reactions (26). Therefore it is evident that the clay has acid sites that convert the ester to amide, N-substituted amide, and nitrile. The origin of these sites was explored to understand the actual mechanism of the reaction.

3.8. *Acidity of the Clay*

The Montmorillonite K10 clay exhibits activity at temperatures above 250°C. So the actual acidic sites that are responsible for the reaction were estimated by NH_3 adsorption at 250°C and the values are given in Table 6. Among all the clay materials examined, Montmorillonite K10 has the maximum acidity. The acidity decreases after the 23 h run. The clay catalysts steamed at 320°C and Na^+-Montmorillonite K10 have low acidity. The used Na^+-Montmorillonite clay is a relatively poor solid acid catalyst.

TABLE 6

Estimation of Acid Sites of Montmorillonite Clays by NH_3 Adsorption at 250°C

No.	Clay catalysts	Nature[a]	NH_3 adsorbed (mmole)/g · cat
1	Montmorillonite K10	Fresh	0.0476
2	Montmorillonite K10	After 23 h run and regenerated[b]	0.0330
3	Montmorillonite K10	Steamed for 6 h at 320°C	0.0320
4	Montmorillonite K10	Steamed for 10 h at 320°C	0.0319
5	Na-Montmorillonite K10	Fresh	0.0270
6	Na-Montmorillonite K10	After 6 h run and regenerated[b]	0.0121

[a] All are used in extruded form.
[b] The catalysts were regenerated by heating at 320°C under the flow of air.

TABLE 7

Influence of Reaction Time on Selectivity to 2, 4, 5[a]

Time on stream, h	Percent conv. of **1**	Selectivity to **2**	**4**	**5**
1	66.7	52.5	3.6	14.0
2	64.0	54.1	4.0	16.5
3	60.0	48.9	4.9	18.9

[a] Montmorillonite K10 = 2 g; **1** : NH_3 = 1 : 1 (molar ratio); N_2 = 30 ml/min; 320°C.

3.9. Turnover Frequency and Performance of Catalyst with Time on Stream

As the acidity values of the different clay catalysts are different the actual evaluation of the catalyst would be to study turnover frequency (TOF) of products (number of moles of product formed per mole of acidic site of catalyst per second) at different periods of reaction. Acidity of the clay is a key factor for the reaction. NH_3 adsorbtion provides the total concentration of acid sites. It is essential to find among Brønsted and Lewis acid sites which type of acid sites are important for formation of **2**, **4**, and **5**. So H-Montmorillonite K10 clay and γ-Al_2O_3 have been examined as catalysts (Table 1). High conversions of **1** are observed on γ-Al_2O_3 and H-Montmorillonite clay. But the selectivity to **2** is similar on these two catalysts. H-Montmorillonite clay is a very strong solid acid (15), compared to Montmorillonite K10 clay, and has higher Brønsted acid sites (27). So very high acidic sites are not suitable for the formation of **2**, compared to acid sites available on Al_2O_3. This suggests the most probable sites in the reaction are Lewis acid sites. High selectivity to **4** + **5** is observed on Montmorillonite K10, HZSM-5, and H-Montmorillonite K10 clay. Among the two amides, selectivity to **5** is always higher than **4** (Table 7). This suggests the possible involvement of very strong Brønsted acid sites in the formation of **5**.

Pyridine adsorption was carried out on Montmorillonite K10 clay in the temperature range 280–340°C and the acid sites were estimated (Table 8) using IR absorbance values at 1542 and 1444 cm^{-1} for the Brønsted and Lewis acid sites, respectively. Figure 3 shows the adsorbed pyridine species on the clay heated at 280°C. Pyridine adsorption can distinguish between the Brønsted and Lewis acid sites (28–29). The characteristic bands of pyridine at 1639, 1542, 1490 cm are observed and indicate the presence of Brønsted acid sites. Bands at 1600, 1490, 1444 cm^{-1} which correspond to pyridine adsorbed on Lewis acid sites are also observed. Ratios of Brønsted acid to Lewis acid sites are calculated from the clay samples activated at different temperatures (Table 8). The ratios of Brønsted to Lewis acid sites, as well as the amount of sites increase with the increase in the clay activation temperature. The increase in concentration of Brønsted acid sites with the increase in temperature is known to occur due to polarisation and dissociation of water (15, 29). When water is removed newer Lewis acid sites are also exposed and activated.

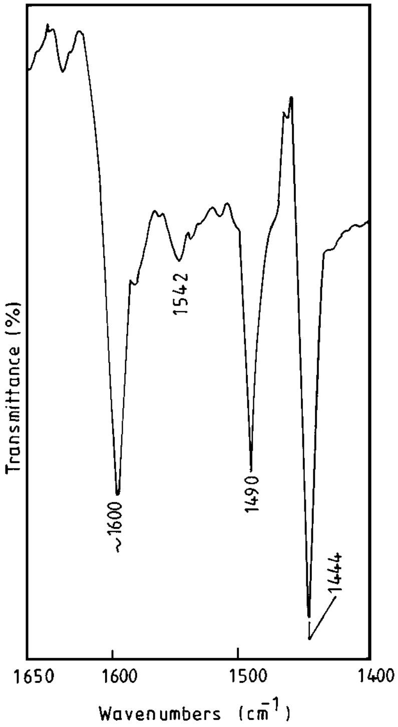


FIG. 3. IR Spectrum of adsorbed pyridine on Montmorillonite K10 clay heated at 280°C.

Figure 4 clearly shows that total TON in a 6 h run of both nitrile and amides increases with the reaction temperature, whereas Fig. 2 shows the selectivity of the products is almost constant after 320°C. The efficiency and stability of the clay catalyst was studied by following the TON of benzonitrile at every hour of the reaction (Fig. 5). There is a gradual fall in the efficiency of the clay catalyst with time on stream. This reveals that deactivation of the catalyst occurred during the course of reaction. It is known that methanol has an affinity for the clay surface (30). So it was thought that the

TABLE 8

Estimation of Acid Sites on Montmorillonite K10 Clay at Different Temperatures

No.	Temp. (°C)	Pyridine adsorbed/g · cat (mmole)	Brønsted acid sites[a] / Lewis acid sites
1	280	0.0683	0.067
2	300	0.0730	0.037
3	320	0.0774	0.049
4	340	0.0825	0.096

[a] Relative proportion of Brønsted and Lewis acid sites is found from IR peaks at 1542 and 1444 cm^{-1}.

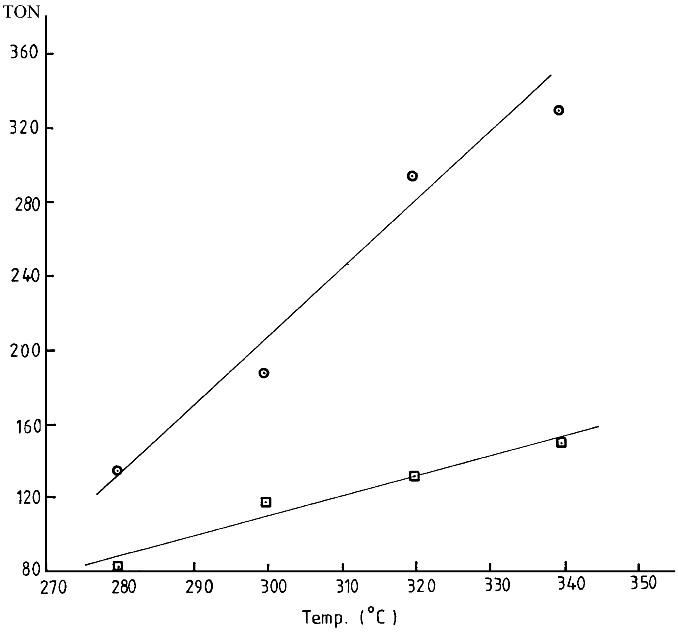


FIG. 4. Turnover number (integral value) vs reaction temperature. Reaction conditions are the same as in Fig. 2: (⊙) **2**; (⊡) (**4** + **5**).

deactivated catalyst could be regenerated by refluxing with methanol. After 13 h continuous run the catalyst was taken out, refluxed with methanol, dried under vacuum, and then used for the conversion of esters to nitrile. An initial increase in activity of the catalyst was observed. However, 1 h after that the catalyst was behaving the same way as before. This suggests that the regeneration of the catalyst by the methanol extraction was not successful. So after an 18 h run the flow of **1** and NH_3 was suspended. The catalyst was purged with N_2 and then in a flow of air it was heated at 320°C for 4 h. Subsequently this catalyst was used for the conversion of ester to nitrile. In this method also the catalyst behaved in a way similar to that in the previous treatment even though the initial activity at 19 h was high. The catalyst, after the reaction, was dried and weighed and showed 8% weight increase. The same catalyst after calcination in air at 320°C shows that organic residue equivalent to 8 wt% increase is removed. This also shows that the above two methods of regeneration of catalyst did not work with Montmorillonite clay catalyst.

Therefore, in order to understand the nature of surface-active sites of the catalyst, the deactivation phenomenon, and the mechanism of reaction, the clay samples were examined by ESCA.

3.10. ESCA Results

The XPS survey spectra of Montmorillonite K10 and its extrudates calcined at 320°C are shown in Fig. 6. An improvement in surface acidity (Si/Al: 4.27 → 3.15, Table 9) of extrudates suitable for reaction indicates enrichment of aluminum atoms on the surface during the extrusion process. Such changes in (Si/Al) values on the surface and in bulk of thermally treated zeolites have been reported by several authors (25, 31, 32).

During the reaction of methyl benzoate with NH_3 the latter is adsorbed on acidic sites of extrudates, resulting in an increase in Si/Al atomic ratio (3.56) up to 280°C with approximately 22% acidic sites covered with basic nitrogen

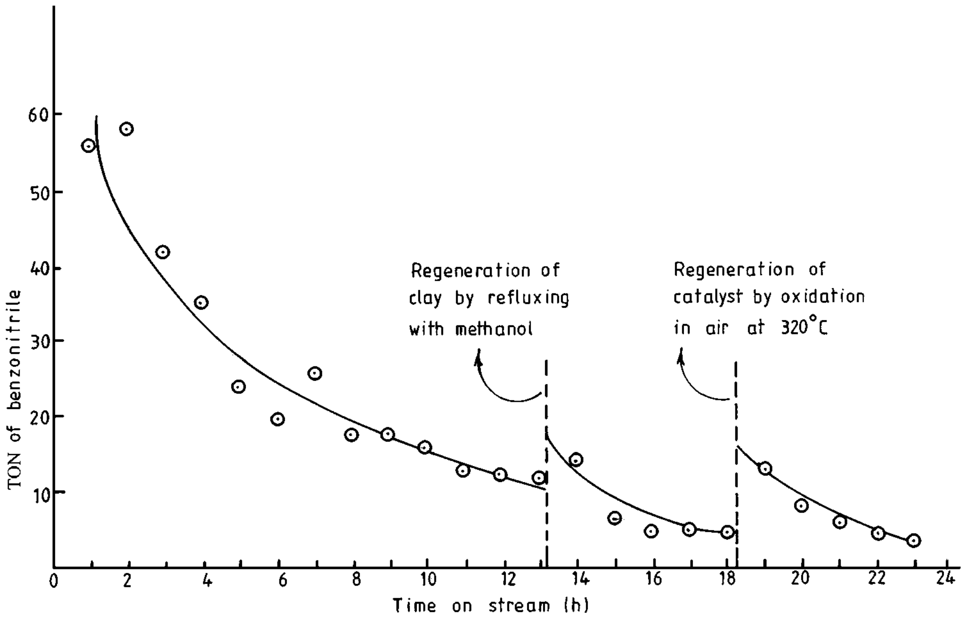


FIG. 5. Efficiency of Montmorillonite clay catalyst with time on stream. Reaction conditions are the same as in Fig. 1.

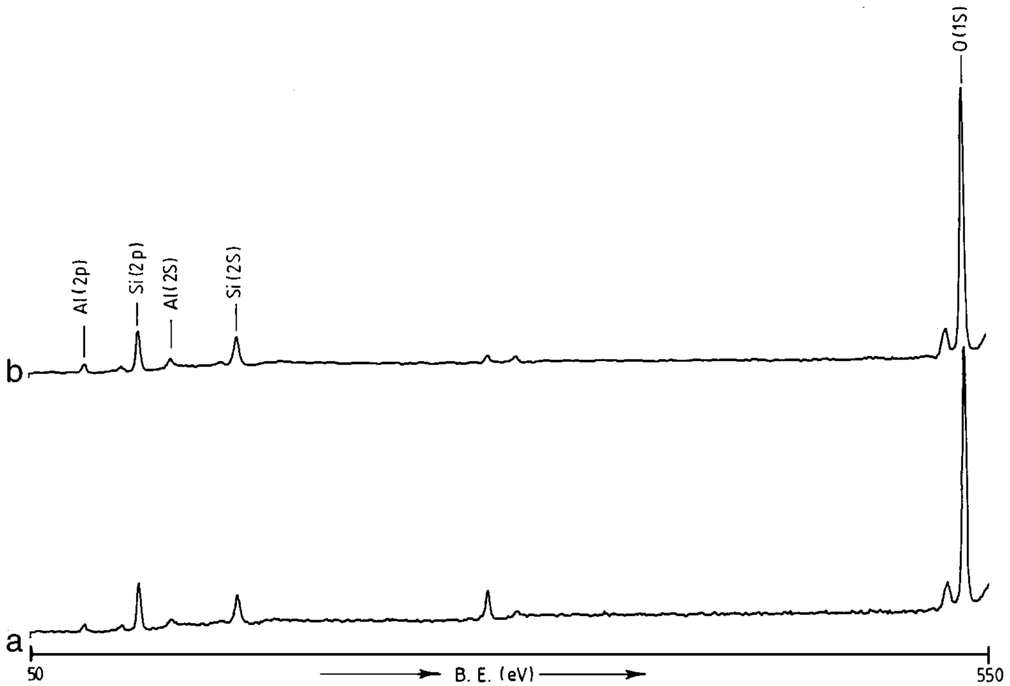


FIG. 6. XPS survey spectra of Montmorillonite (a) powder and (b) extrudates.

compounds. As the reaction temperature is increased to 320°C and then to 340°C, weakly bonded nitrogen and its compounds desorb from the surface, resulting in a decrease in Si/Al values to 3.31 and 3.17, respectively. However, the amount of the nitrogen bonded to aluminum atoms on the surface was found to be constant ($\approx$15%). This behaviour of the catalyst can be correlated with the selectivity of nitriles in the reaction which increases initially up to 320°C and then becomes constant above 320°C.

TABLE 9

Surface Quantitative Results for Extrudates after Various Treatments (Atomic Ratio)

Sample	Si/Al	N/Al	Na/Al
Powder Montmorillonite	4.27	—	—
Extrudates—fresh	3.15	—	—
Extrudates			
280°C after 6 h run	3.56	0.22	—
320°C after 6 h run	3.31	0.15	—
340°C after 6 h run	3.17	0.15	—
320°C after 13 h run	3.41	Not estimated	—
320°C after 23 h run	3.62	0.87[a]	—
Extrudates—regenerated at 340°C for 6 h after 23 h run at 320°C	3.67	0.56[a]	
Na exchanged extrudates, fresh	3.31	—	0.23
used (320°C after 6 h run)	3.68	—	0.38
Fresh extrudates dealuminated with steam (320°C for 6 h)	3.44	—	—
Fresh extrudates dealuminated with steam (320°C for 10 h)	3.47	—	—

[a] N(1S) B.E. = 400 eV.

In order to study deactivation behaviour of the catalyst, the Si/Al atomic ratio on the surface were estimated for catalyst runs for 6, 13, and 23 h at 320°C. An increase in Si/Al ratio from 3.15 to 3.31, 3.41, and then to 3.62 indicates surface dealumination and, hence, decrease in acidity. It can also be seen from Fig. 7 that a prolonged (23 h) exposure of the catalyst to reactants results in a large accumulation of carbon and nitrogen compounds on the surface.

The broadening in N(1S) photoelectron lines of used catalyst shown in Figs. 8b and 8c indicate the presence of more than one nitrogen species on its surface. An active catalyst (6 h run) has N(1S) binding energy close to the $\mathrm{NH_3}$ adsorbed in fresh catalyst and deactivated catalyst has N(1S) binding energy close to the amide ($-\mathrm{CONH_2}$) functionalities. In fact the binding energy values and line shape data of N(1S) photoelectron lines suggest the formation of ammonium ion ($\mathrm{NH_4^+}$) (33) and amide ($\mathrm{CONH_2}$) functionalities (34) during the reaction; $\mathrm{NH_4^+}$ ions participate in the reaction while the presence of an amide on the surface leads to deactivation of the catalyst. The catalyst regenerated at 340°C after a 23 h run at 320°C gives N/Al = 0.56 with N(1S) binding energy of 400 eV which is charactristic of benzamide. Thus accumulation of amides on the surface and decrease in surface acidity of the catalyst are the main reasons of catalyst deactivation.

In $\mathrm{Na^+}$-Montmorillonite (extrudates), it is presumed that sodium atoms are exchanged with the acidic sites of Montmorillonite. For these extrudates the estimated

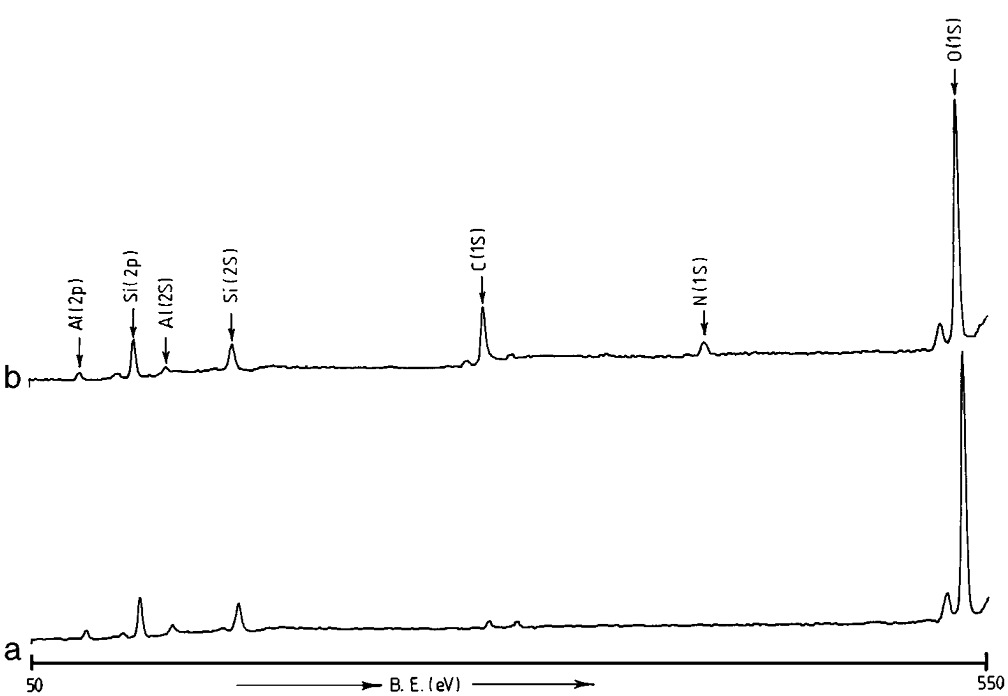


FIG. 7. XPS survey scans of (a) fresh extrudates and (b) used extrudates (23 h) of Montmorillonite K10.

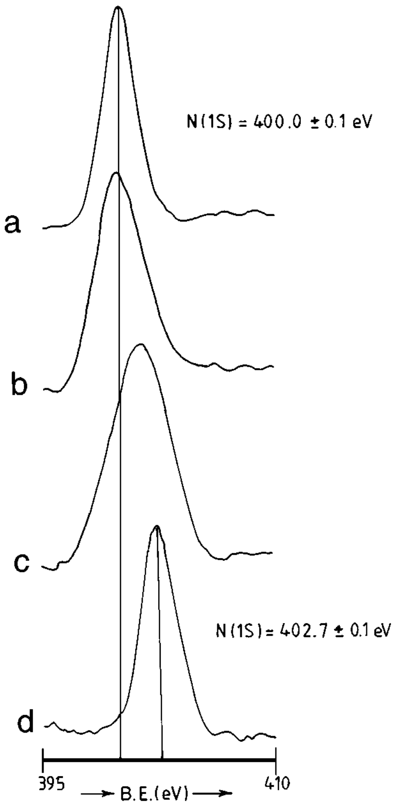


FIG. 8. N(1S) photoelectron lines of (a) benzamide, (b) extrudates of Montmorillonite K10 after 23 h run, (c) extrudates after 6 h run, (d) fresh extrudates after adsorption of NH_3.

value of the Si/Al ratio was 3.31 and the Na/Al atomic ratio on the surface was 0.23 (Table 9). Thus acidity of these extrudates is lower (Table 6), compared to fresh extrudates, which is also supported by their catalytic data. When Na^+-Montmorillonite (extrudates) were used in the reaction, sodium enrichment on the surface takes place (Na/Al = 0.38) and, hence, surface acidity further goes down, resulting in the poor activity of exchanged extrudates on use. XPS survey scans of fresh and used Na^+-Montmorillonite (extrudates) are shown in Fig. 9. The binding energy of Na(1S) photoelectron line in these extrudates is 1073 ± 0.2 eV (Fig. 10) which is close to the reported value (35) for NaY zeolite. It is worth mentioning that nitrogen species were not detected on the surface of used Na^+-Montmorillonite (extrudates).

As sodium and nitrogen are adsorbed on acidic sites of alumina in Montmorillonite, it is possible to correlate the effective active sites on the surface of clay extrudates to catalytic activity as shown in Table 10. Thus acidic sites attached to aluminum atoms of clay are responsible for activity behaviour of the catalyst. Steam dealumination of fresh extrudates was carried out for 6 and 10 h to see the extent of aluminum atoms leaching out from the surface of the silica-alumina framework. An increase in Si/Al ratio from 3.15 to 3.44 and 3.47 (Table 9) indicates that 8.5% of aluminum atoms are leaching out and dealumination is nearly complete in 6 h steaming of extrudates at 320°C. This is supported by TPD data shown in Table 6 which gives nearly the same ammonia adsorption values for these two dealuminated extrudates.

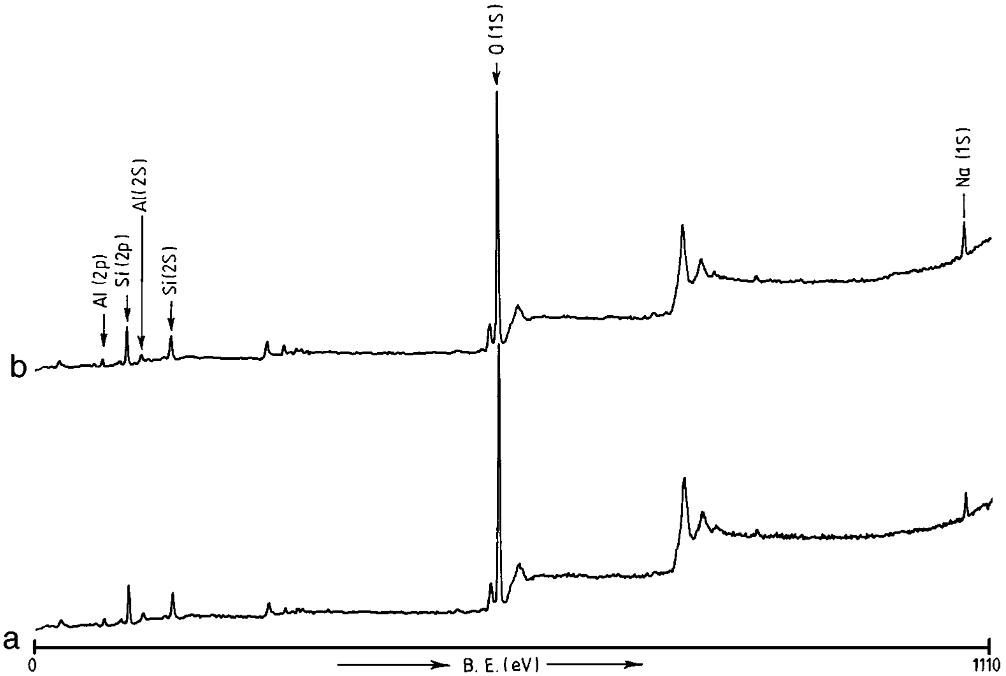


FIG. 9. XPS survey spectra of Na^+-Montmorillonite K10 (extrudates) in (a) fresh and (b) used stage.

3.11. Mechanism

The above studies clearly indicate the acid sites responsible for the catalysis are on the aluminium atoms. We have observed that Brønsted acid sites and Lewis acid sites (predominantly) are present on Montmorillonite clay. The facile reaction of **1** and NH_3 on γ-Al_2O_3 to give **2** and the similar trend on clay suggests the participation of Lewis acid sites in this reaction. It is reported on similar solid acid catalyst SO_4^{2-}/ZrO_2 dehydration of amide to nitrile is catalyzed by Lewis acid sites (36). So it is most probable that formation of **2** is catalyzed by Lewis acid sites (Al^{3+}) of clay. Involvement of both Brønsted and Lewis acid sites in the formation of **4** cannot be ruled out. In presence of H-Montmorillonite K10 and H-ZSM5 the formation of **2** is decreased with the increase in formation of **4** and **5** (predominantly). On Montmorillonite K10 also the predominant formation of **5** suggests it is catalyzed by Brønsted acid sites.

The deactivation is clearly due to loss of acidity on the surface of clay because of dealumination by water at 320°C. This loss of aluminum atoms is estimated to be 8.5 wt%; i.e., every one aluminium atom out of 11–12 atoms is leached out. This results in accumulation of negative charges on the clay. The amide derivatives can strongly adsorb on the clay to neutralise the charges. In the process some more

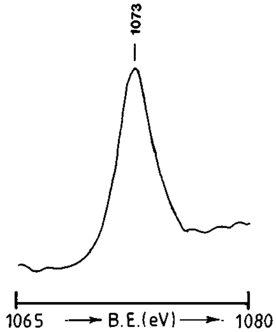


FIG. 10. Na(1S) photoelectron spectrum of Na^+-Montmorillonite K10 (extrudates).

TABLE 10

Correlation of Catalytic Data with Active Sites Estimated from Surface Spectroscopic Data

Sample	Si/Al atomic ratio	Effective active sites (at%)	Ratio[a]	Activity[b]	Ratio[c]
1. Fresh extrudates	3.15	8.26	1.24	86.4	1.21
2. Used extrudates (6 h)	3.31	6.80		69.7	
3. Na^+ exchanged fresh extru.	3.31	6.10	1.40	67.8	1.36
4. Used Na^+ exch. extrudates (6 h)	3.68	4.50		48.4	

[a] Active sites of fresh extrudates/active sites of used extrudates.

[b] Turnover of nitrile per hour activity taken after 1 h stabilization in case of fresh extrudates.

[c] Activity of fresh extrudates/activity of used extrudates.

acid sites become inaccessible to the reactants for further reaction to take place.

4. CONCLUSIONS

It has been shown that Montmorillonite K10 clay is an active catalyst in the production of benzonitrile [**2**], benzamide [**4**], and N-methyl benzamide [**5**] from methyl benzoate on reaction with NH_3 in the temperature range 280–340°C. Various reaction parameters which influence the conversion of ester and the selectivity of the products have been studied. This catalyst is equally active for the conversion of other esters into corresponding nitriles. From NH_3, as well as pyridine adsorption, the amount of acidic sites participating in the reaction has been estimated. There is slow and gradual deactivation of the clay catalyst during the reaction.

ESCA study of the clay extrudates at various stages of preparation and reaction is carried out. The surface acidity of the Montmorillonite increases in the extrusion process because of surface enrichment of aluminum atoms. During the reaction NH_3 is adsorbed on the acidic $>$Al–OH sites and forms ammonium ions (NH_4^+). These participate in the reaction. The deactivation of the catalyst was mainly due to dealumination by water produced in the reaction and accumulation of organic residue containing amide groups on the surface of the clay. As a result of this study it is possible to calculate effective acidic sites on the clay surface and, hence, a correlation with the performance of the catalyst is possible.

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