# Surface acidity and catalytic activity of mixed Fe-Al and Cr-Al pillared montmorillonites

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The incorporation of transition metal oxide pillars such as those of iron and chromium along with $Al_2O_3$ pillars within the interlayers of a montmorillonite clay is investigated. The surface acidity of these catalysts has been evaluated for the first time employing the equilibrium adsorption of an electron donor, perylene, and the results are compared with those obtained by temperature programmed desorption of ammonia. The principle is based on the ability of a catalyst surface site to accept a single electron from an electron donor like perylene to form charge transfer complexes and the amount of adsorbed species is measured quantitatively by UV-vis spectroscopy. Finally, an attempt has been made to correlate the acidity determined by the two independent methods and the catalytic activity of present systems in the benzoylation of toluene with benzoyl chloride. Incorporation of Fe and Cr has changed the properties of Al pillared montmorillonite. Fe pillared systems have been found to be very good catalysts for benzoylation reaction.

Extensive research on pillared smectites has proven their applications in the field of heterogeneous catalysis and adsorption[1-5]. Several studies have shown that pillared clays with single metal oxide clusters as pillars in the inter layer region are active catalysts for cracking reactions, alkylation reactions and hydrotreating applications[6-9]. Efforts to improve the thermal stability and catalytic properties of the single oxide pillared clays have led to the preparation of mixed oxide pillared clays[10]. Zr and Al oligomers are among the most widely used pillaring agents for the preparation of single pillared clays[11,12]. Other robust cations used to pillar smectites include those of iron[3], chromium[13,14] and titanium[15]. It has been observed that mixed oxide pillared materials exhibit improved surface area and surface acidity with respect to the single oxide pillared materials[16-19].

The present work reports the effect of incorporation of transition metal oxide pillars such as those of iron and chromium along with $Al_2O_3$ pillars within the interlayers of a montmorillonite clay. The surface acidity of the various pillared clays are clearly examined by two methods viz. the temperature programmed desorption of ammonia and electron accepting studies using perylene as the electron donor. As far as we know, there are hardly any reports on the surface acidity measurement of pillared clays by adsorption techniques using perylene as the electron donor. Useful information regarding the Lewis acidity in presence of Bronsted acidity can be obtained using this procedure[20]. The principle is based on the ability of a catalyst surface site to accept a single electron from an electron donor like perylene to form charge transfer complexes and the amount of adsorbed species is measured quantitatively by spectroscopic studies[21,22]. Finally, an attempt has been made to correlate the acidity determined by the two independent methods and the catalytic activity of present systems in the benzoylation of toluene with benzoyl chloride.

## Material and Methods

### Preparation of pillared montmorillonites

The starting material kindly supplied by Fluka (Montmorillonite, KSF) had the chemical composition (Na-0.83; Mg-1.98; Al-17.94; Si-50.78; S-14.76; K-1.59; Ca-2.97; Fe-9.15) in wt%. The initial step of the preparation of the various pillared montmorillonites is the preparation of corresponding pillaring agents. Aluminium nitrate solution (0.2 *M*) was partially hydrolysed using 0.3 *M* sodium carbonate as the base at a base/metal ratio 2.0 under vigorous stirring at 343 K for two h and the stirring is continued for six h at room temperature. The pillaring agent was flushed with nitrogen to free $CO_2$ from the solution and kept for ageing for one day at room temperature. In the next step, a previously prepared suspension (1 wt%) of the parent montmorillonite was treated with the pillaring solution for six h at 343 K. $M^{3+}$ to clay ratio was maintained as 20 mmoles/g of the clay in the final reaction mixture. After reaction, the material was washed free of nitrate and until

flocculation appeared. It was then dried at 383 K, followed by controlled calcination in dry air at 673 K for 5 h to get aluminium pillared montmorillonite (AlPM) catalyst.

A similar method was adopted for the preparation of iron pillared montmorillonite (FePM). The pillaring agent was prepared by partially hydrolyzing 0.2 $M$ iron nitrate with 0.3 $M$ sodium carbonate until the base to metal ratio reached 2.0 at 343 K for 2 h and the stirring was continued for six hours. Room temperature aged (24 h) pillaring agent was added to 1 wt% suspension of the parent clay and stirred for six h at 343 K. Same molar solutions were used for preparing the pillaring agent for chromium pillared montmorillonite (CrPM). But the pillaring solution was prepared at 368 K and the warm solution was used for pillaring[23] the clay.

Mixed Fe-Al and Cr-Al pillared montmorillonites were prepared for Fe (Cr)/Al ratios 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0. $Fe(NO_3)_3$ or $Cr(NO_3)_3$ (0.2 $M$) was added to 0.2 $M$ $Al(NO_3)_3$ at the desired amount before partial hydrolysis with sodium carbonate. Preparation of mixed Fe-Al systems was carried out by following the same route as that of Fe PM and that of mixed Cr-Al PM was carried out as that of CrPM. The mixed systems are represented as $FeAl_x$ PM and $CrAl_x$ PM where x denotes the Fe (Cr)/Al ratio.

*Characterisation*

The chemical compositions of all the pillared samples were determined by the electron dispersive X-ray analysis (EDX) performed over an EDX-JEM-35 (JEOL Co. link system AN-1000, Si-Li detector, Sensitivity > 0.1 weight %) instrument. XRD patterns of the various catalysts were taken using Ni filtered Cu $K_\alpha$ radiation. Measurement of surface area of the catalysts were performed over a Micromeritics Flowprep-060 (Model-236/ 0001/ 00) apparatus using nitrogen gas as adsorbate. Previously activated samples were degassed at 200°C under nitrogen flow for two h and brought to liquid nitrogen temperature. Then nitrogen gas was adsorbed on the sample at various relative pressures $(P/P_0)$ from 0.1 to 0.5. Surface area was measured using the BET equation. Total pore volume was also measured using the same Micromeritics apparatus by the adsorption of nitrogen at $P/P_0$ 0.9 and at liquid nitrogen temperature. Acidity measurements were done using two independent techniques viz. determining surface electron accepting properties using perylene adsorption method and temperature programmed desorption (TPD) of

ammonia. Different concentrations of perylene in a non-aqueous medium such as benzene was allowed to stir with about 0.5 g of catalyst. The difference in concentration before and after adsorption was determined using UV-vis spectroscopy ($\lambda_{max}$ of perylene in benzene solution is 439 nm).

Temperature programmed desorption of ammonia is based on calculating the amount of desorbing ammonia which is adsorbed on the solid by heating at a programmed rate. About 0.75 g of the previously activated catalyst was first degassed by heating in a stream of nitrogen at 573 K. It was then cooled to room temperature and ammonia was adsorbed. The catalyst was then heated through a temperature programme in nitrogen flow. At each interval of 100 K, the ammonia desorbed was trapped using nitrogen as the carrier gas in a stoppered conical flask containing an excess of 0.025 $N$ sulphuric acid solution for the temperature range 373 K-873 K. Then the trapped ammonia was evaluated by volumetric determination of the excess sulphuric acid using 0.025 $N$ NaOH. The amount of ammonia desorbed was distributed in the weak (373-473 K), medium (473-673 K) and strong regions (673-873 K).

The liquid phase benzoylation reaction was carried out over 0.1 g of the catalysts in a 100 mL RB flask immersed in an oil bath for one hour at the boiling temperature of toluene. The toluene: benzoyl chloride molar ratio was maintained at 5:1 taking 10.62 mL of toluene and 2.3 mL of benzoyl chloride. The catalyst to substrate ratio is 0.1 g/9.2 g of toluene. The products were analysed using a gas chromatograph (Chemito GC 8610) fitted with an SE 30 column and FID.

**Results and Discussion**

*Textural properties of pillared montmorillonites*

From our results we observed that the properties of the various pillared clays formed by the ion exchange reaction of parent montmorillonite with various metal ion solutions depended critically on the nature of the intercalation solution. Tables 1 and 2 summarise the surface areas and pore volumes of mixed Fe-Al pillared montmorillonites and mixed Cr-Al pillared montmorillonites respectively. Tables 3 and 4 give the $d(001)$ spacing and relative intensity. The surface areas of the pillared samples were determined using BET equation. The parent montmorillonite has only a very low surface area of 6 $m^2/g$ and a $d(001)$ spacing of 9.82 Å. Pillaring of KSF leads to a substantial increase of BET surface area from 6 $m^2/g$ to a range

of 100-200 m²/g. AlPM calcined at 400°C has a BET surface area of 102.5 m²/g and d spacing of 16.74 Å. An attempt to introduce iron in order to obtain a mixed pillar system resulted in slight variation in $d$ spacing. For FePM, the $d$ spacing is 15.48 Å. For mixed Fe-AlPMs, $d$ values intermediate between that of AlPM and FePM are obtained. This is in agreement with the results obtained for Zhao *et al*.[24], though the difference in $d$ spacing between the various mixed Fe-Al pillared montmorillonites is less prominent in our work. At low Fe/Al ratios, the $d$ spacing is more close to that of Al PM and at high Fe/Al ratios (0.5 and 1.0), the $d$ spacing is closer to that of FePM. This suggests that the structure of the polymeric pillaring species with high Fe/Al ratio resembles that of iron oligomer and at low Fe/Al ratios the structure resembles that of Al oligomer[24,25]. The surface area of mixed Fe-AlPM increases gradually for Fe/Al ratio 0.1 to 0.5 from 83 m²/g to 198 m²/g and for FeAl$_{1.0}$PM, the surface area reduces to 131.2 m²/g. While examining the mixed Fe-Al systems it is clear that increase in surface area is consistent with the relative intensities of $d$(001). The intensity for the

peak increases up to the ratio 0.5 and then decreases, so as the efficiency of pillaring and hence surface area.

For mixed Cr-Al PMs, the surface area ranges from 90m²/g to 131m²/g. The relative intensities for the $d$ (001) peak is depicted in Table 4. The variation in surface area by changing the Cr/Al ratio is not so prominent as in the case of mixed Fe-Al PMs. Another interesting observation is that calcining at higher temperatures resulted in higher surface area with a subsequent increase in pore volume. This suggests that calcination at higher temperatures creates more and more pores in the interior of the clay, which resulted in higher surface area. This is in contrast to Fe-Al mixed systems.

## Loading of pillaring species

The chemical compositions of mixed Fe-Al pillared montmorillonites determined by EDX analysis are shown in Table 5. The parent montmorillonite has an iron weight percentage of 10.73. The silicon and aluminium weight percentages are 59.57 and 21.05 respectively. Pillaring of montmorillonite with Al poly oxocations (AlPM) increases the weight percentage of Al from 21.05 to 29.51 %. Thus an

Table 1—Surface area, pore volume and $d$ (001) of mixed Fe-Al pillared montmorillonites.

| Catalyst | BET Surface area ( m²/ g ) 400°C | 500°C | Pore volume (cm³/g) (400°C) |
|---|---|---|---|
| KSF | 6.60 | - | 0.0043 |
| AlPM | 102.50 | 88.62 | 0.0888 |
| FeAl$_{0.1}$PM | 83.01 | 61.56 | 0.0559 |
| FeAl$_{0.2}$PM | 103.70 | 99.87 | 0.0863 |
| FeAl$_{0.3}$PM | 123.80 | 116.12 | 0.0913 |
| FeAl$_{0.4}$PM | 146.80 | 139.81 | 0.1213 |
| FeAl$_{0.5}$PM | 198.00 | 188.60 | 0.1723 |
| FeAl$_{1.0}$PM | 131.20 | 101.90 | 0.0922 |
| FePM | 188.67 | 169.11 | 0.1435 |

Table 2—Surface area, pore volume and $d$ (001) of mixed Cr-Al pillared montmorillonites.

| Catalyst | BET Surface area (m²/g) 400°C | 500°C | Pore volume (cm³/g) 400°C | 500°C |
|---|---|---|---|---|
| AlPM | 102.50 | 88.62 | 0.0888 | 0.0784 |
| CrAl$_{0.1}$PM | 106.49 | 121.21 | 0.0722 | 0.0799 |
| CrAl$_{0.2}$PM | 110.54 | 124.31 | 0.0748 | 0.0802 |
| CrAl$_{0.3}$PM | 107.59 | 118.21 | 0.0712 | 0.0781 |
| CrAl$_{0.4}$PM | 113.43 | 131.18 | 0.0749 | 0.0831 |
| CrAl$_{0.5}$PM | 112.19 | 129.21 | 0.0752 | 0.0811 |
| CrAl$_{1.0}$PM | 70.83 | 92.36 | 0.0521 | 0.0684 |
| CrPM | 96.33 | 113.73 | 0.0699 | 0.0731 |

Table 3—XRD Data of mixed Fe-Al pillared montmorillonites.

| Catalyst | 2θ (degree) | $d$ (001) (Å) | Relative intensity |
|---|---|---|---|
| KSF | 9.00 | 9.82 | 87.42 |
| AlPM | 5.26 | 16.74 | 38.23 |
| FeAl$_{0.1}$PM | 5.40 | 16.38 | 40.45 |
| FeAl$_{0.2}$PM | 5.54 | 16.01 | 49.23 |
| FeAl$_{0.3}$PM | 5.46 | 16.14 | 51.36 |
| FeAl$_{0.4}$PM | 5.48 | 16.11 | 59.32 |
| FeAl$_{0.5}$PM | 5.66 | 15.62 | 69.54 |
| FeAl$_{1.0}$PM | 5.53 | 15.98 | 57.21 |
| FePM | 5.72 | 15.48 | 69.21 |

Table 4—XRD Data of mixed Cr-Al pillared montmorillonites.

| Catalyst | 2θ (degree) | $d$ (001) (Å) | Relative intensity |
|---|---|---|---|
| AlPM | 5.26 | 16.74 | 38.23 |
| CrAl$_{0.1}$PM | 5.20 | 17.01 | 42.32 |
| CrAl$_{0.2}$PM | 5.17 | 17.04 | 43.65 |
| CrAl$_{0.3}$PM | 5.10 | 17.32 | 42.66 |
| CrAl$_{0.4}$PM | 5.01 | 17.61 | 43.00 |
| CRAl$_{0.5}$PM | 5.00 | 17.66 | 43.25 |
| CrAl$_{1.0}$PM | 4.99 | 17.73 | 39.22 |
| CrPM | 4.87 | 18.10 | 41.36 |

excess of 8.46 % of Al is fixed by the pillared solid. The drastic decrease of Ca from 3.48 to 0.04 % during this pillaring process indicates that the main cation exchanged was $Ca^{2+}$.

Pillaring of montmorillonite with Fe poly cations (FePM) increases its iron content from 10.73 to 29.01%. Various pillaring agents were prepared by the co-hydrolysis of $Al(NO_3)_3$ and $Fe(NO_3)_3$ in the Fe/Al ratios 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0 with sodium carbonate as base. Pillaring agent containing both aluminium and iron poly oxocations was used for pillaring the montmorillonite. Pillaring of the montmorillonite with a mixture of Fe and Al poly cations increases both Al content and iron content. Maximum uptake of iron was for $FeAl_{0.5}PM$. The uptake of iron by the solid for Fe/Al ratio of 1.0 is found to be less than that at a ratio of 0.5. The pillaring agent with lower Fe/Al ratios such as 0.1 or 0.2 resembles more to aluminium pillaring agent and the amount of iron incorporated into the solid is less. At a higher Fe/Al ratio of 0.5, more iron is incorporated into the clay sheets than aluminium. However, at a much higher Fe/Al ratio of 1.0, the amount of iron introduced into the clay structure was less than that for the ratio 0.5.

Table 6 shows the chemical composition of Cr-pillared and mixed Cr-Al pillared montmorillonites. When the parent montmorillonite is pillared with chromium poly cations, 19.20 % of chromium is fixed into the solid. For Al-pillared montmorillonite, excess of aluminium introduced into the solid as a result of pillaring process is 8.46%. For the mixed Cr-Al pillared montmorillonite, chromium is introduced along with aluminium. The chromium weight percentage reached a maximum of 11.73 for Cr-$Al_{0.5}PM$. However, further increase of Cr/Al ratio from 0.5 to 1.0, only reduced the chromium content.

## Acidity determinations
### (a) Electron accepting properties

Perylene is adsorbed at room temperature from a solution in benzene on the various samples. The pale yellow colour of the AlPM changed to a mottled lavender colour due to the adsorption of perylene on the surface. Due to the dark brown colour of Fe-AlPMs and dark green colour of Cr-AlPMs the change in colour due to adsorption of perylene was not clearly visible. Perylene being an electron donor donates electron to the Lewis surface sites and gets adsorbed as perylene radical cation[20]. Thus after

Table 5—Chemical composition of the various elements in mixed Fe-Al pillared montmorillonites

| Catalyst | Weight percentages | | | | | | |
|---|---|---|---|---|---|---|---|
| | Si | Al | Fe | Ca | K | Mg | Na |
| KSF | 59.57 | 21.05 | 10.73 | 3.48 | 1.86 | 2.32 | 0.97 |
| AlPM | 56.43 | 29.51. | 10.20 | 0.04 | 1.59 | 1.86 | 0.35 |
| $FeAl_{0.1}PM$ | 57.09 | 27.02 | 12.81 | 0.02 | 1.10 | 1.39 | 0.57 |
| $FeAl_{0.2}PM$ | 55.58 | 26.92 | 14.60 | 0.10 | 1.50 | 1.39 | 0.37 |
| $FeAl_{0.3}PM$ | 54.63 | 24.01 | 17.41 | 0.08 | 1.57 | 1.39 | 0.90 |
| $FeAl_{0.4}PM$ | 55.01 | 22.10 | 20.08 | 0.02 | 1.10 | 1.07 | 0.62 |
| $FeAl_{0.5}PM$ | 50.97 | 21.63 | 24.44 | 0.04 | 0.79 | 1.58 | 0.52 |
| $FeAl_{1.0}PM$ | 53.68 | 22.42 | 19.61 | 0.08 | 1.47 | 1.93 | 0.79 |
| FePM | 47.49 | 20.37 | 29.01 | 0.09 | 1.10 | 1.57 | 0.36 |

Table 6—Chemical composition of the various elements in mixed Cr-Al pillared montmorillonites

| Catalyst | Weight percentages | | | | | | |
|---|---|---|---|---|---|---|---|
| | Si | Al | Fe | Cr | Ca | K | Mg | Na |
| AlPM | 56.43 | 29.51. | 10.20 | 0.00 | 0.04 | 1.59 | 1.86 | 0.35 |
| $CrAl_{0.1}PM$ | 56.78 | 27.09 | 10.73 | 2.08 | 0.10 | 1.38 | 1.79 | 0.05 |
| $CrAl_{0.2}PM$ | 56.50 | 24.95 | 10.85 | 4.35 | 0.23 | 1.43 | 1.67 | 0.00 |
| $CrAl_{0.3}PM$ | 57.89 | 23.82 | 9.83 | 5.21 | 0.21 | 1.19 | 1.83 | 0.01 |
| $CrAl_{0.4}PM$ | 57.32 | 22.26 | 9.11 | 6.54 | 0.10 | 1.51 | 1.92 | 0.24 |
| $CrAl_{0.5}PM$ | 57.94 | 22.88 | 9.68 | 11.73 | 0.00 | 1.34 | 1.82 | 0.01 |
| $CrAl_{1.0}PM$ | 55.31 | 23.98 | 10.21 | 7.10 | 0.24 | 1.21 | 1.75 | 0.20 |
| CrPM | 50.80 | 17.71 | 9.15 | 19.20 | 0.25 | 1.19 | 1.73 | 0.05 |

excess of 8.46 % of Al is fixed by the pillared solid. The drastic decrease of Ca from 3.48 to 0.04 % during this pillaring process indicates that the main cation exchanged was $Ca^{2+}$.

Pillaring of montmorillonite with Fe poly cations (FePM) increases its iron content from 10.73 to 29.01%. Various pillaring agents were prepared by the co-hydrolysis of $Al(NO_3)_3$ and $Fe(NO_3)_3$ in the Fe/Al ratios 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0 with sodium carbonate as base. Pillaring agent containing both aluminium and iron poly oxocations was used for pillaring the montmorillonite. Pillaring of the montmorillonite with a mixture of Fe and Al poly cations increases both Al content and iron content. Maximum uptake of iron was for FeAl₀.₅PM. The uptake of iron by the solid for Fe/Al ratio of 1.0 is found to be less than that at a ratio of 0.5. The pillaring agent with lower Fe/Al ratios such as 0.1 or 0.2 resembles more to aluminium pillaring agent and the amount of iron incorporated into the solid is less. At a higher Fe/Al ratio of 0.5, more iron is incorporated into the clay sheets than aluminium. However, at a much higher Fe/Al ratio of 1.0, the amount of iron introduced into the clay structure was less than that for the ratio 0.5.

Table 6 shows the chemical composition of Cr-pillared and mixed Cr-Al pillared montmorillonites. When the parent montmorillonite is pillared with chromium poly cations, 19.20 % of chromium is fixed into the solid. For Al-pillared montmorillonite, excess of aluminium introduced into the solid as a result of pillaring process is 8.46%. For the mixed Cr-Al pillared montmorillonite, chromium is introduced along with aluminium. The chromium weight percentage reached a maximum of 11.73 for Cr-Al₀.₅PM. However, further increase of Cr/Al ratio from 0.5 to 1.0, only reduced the chromium content.

*Acidity determinations*

*(a) Electron accepting properties*

Perylene is adsorbed at room temperature from a solution in benzene on the various samples. The pale yellow colour of the AlPM changed to a mottled lavender colour due to the adsorption of perylene on the surface. Due to the dark brown colour of Fe-AlPMs and dark green colour of Cr-AlPMs the change in colour due to adsorption of perylene was not clearly visible. Perylene being an electron donor donates electron to the Lewis surface sites and gets adsorbed as perylene radical cation[20]. Thus after

Table 5—Chemical composition of the various elements in mixed Fe-Al pillared montmorillonites

| Catalyst | Weight percentages | | | | | | |
|---|---|---|---|---|---|---|---|
| | Si | Al | Fe | Ca | K | Mg | Na |
| KSF | 59.57 | 21.05 | 10.73 | 3.48 | 1.86 | 2.32 | 0.97 |
| AlPM | 56.43 | 29.51. | 10.20 | 0.04 | 1.59 | 1.86 | 0.35 |
| FeAl₀.₁PM | 57.09 | 27.02 | 12.81 | 0.02 | 1.10 | 1.39 | 0.57 |
| FeAl₀.₂PM | 55.58 | 26.92 | 14.60 | 0.10 | 1.50 | 1.39 | 0.37 |
| FeAl₀.₃PM | 54.63 | 24.01 | 17.41 | 0.08 | 1.57 | 1.39 | 0.90 |
| FeAl₀.₄PM | 55.01 | 22.10 | 20.08 | 0.02 | 1.10 | 1.07 | 0.62 |
| FeAl₀.₅PM | 50.97 | 21.63 | 24.44 | 0.04 | 0.79 | 1.58 | 0.52 |
| FeAl₁.₀PM | 53.68 | 22.42 | 19.61 | 0.08 | 1.47 | 1.93 | 0.79 |
| FePM | 47.49 | 20.37 | 29.01 | 0.09 | 1.10 | 1.57 | 0.36 |

Table 6—Chemical composition of the various elements in mixed Cr-Al pillared montmorillonites

| Catalyst | Weight percentages | | | | | | |
|---|---|---|---|---|---|---|---|
| | Si | Al | Fe | Cr | Ca | K | Mg | Na |
| AlPM | 56.43 | 29.51. | 10.20 | 0.00 | 0.04 | 1.59 | 1.86 | 0.35 |
| CrAl₀.₁PM | 56.78 | 27.09 | 10.73 | 2.08 | 0.10 | 1.38 | 1.79 | 0.05 |
| CrAl₀.₂PM | 56.50 | 24.95 | 10.85 | 4.35 | 0.23 | 1.43 | 1.67 | 0.00 |
| CrAl₀.₃PM | 57.89 | 23.82 | 9.83 | 5.21 | 0.21 | 1.19 | 1.83 | 0.01 |
| CrAl₀.₄PM | 57.32 | 22.26 | 9.11 | 6.54 | 0.10 | 1.51 | 1.92 | 0.24 |
| CrAl₀.₅PM | 57.94 | 22.88 | 9.68 | 11.73 | 0.00 | 1.34 | 1.82 | 0.01 |
| CrAl₁.₀PM | 55.31 | 23.98 | 10.21 | 7.10 | 0.24 | 1.21 | 1.75 | 0.20 |
| CrPM | 50.80 | 17.71 | 9.15 | 19.20 | 0.25 | 1.19 | 1.73 | 0.05 |

adsorption the concentration of perylene in the solution decreases. This decrease is found out using absorbance measurements and will correspond to the amount of perylene getting adsorbed on the surface, which in turn corresponds to the Lewis acidity of the system. As the concentration of perylene used for adsorption is increased, the amount of perylene getting adsorberd on the solid surface also increases. But after a particular concentration, the amount of perylene adsorbed remains constant. This amount is referred to as the limiting amount. The limiting amount of perylene indicates the surface electron accepting capacity or in other words, the Lewis acidity of the solid sample. The limiting amount is represented graphically by plotting the amount of perylene adsorbed against its equilibrium concentration when a Langmuir type of adsorption curve is obtained. Figures 1 and 2 show the electron accepting capacities of the various pillared samples. For mixed Fe-Al systems, the electron accepting capacities increase as the iron content increases. The limiting amount observed for AlPM is less than that of FePM. A gradual increase in limiting amount from the ratio 0.1 to 1.0 (though the difference is not so significant for ratios 0.2, 0.3 and 0.4) suggests that more and more electron accepting centers are located at iron oxide pillars. However, no such gradation can be pointed out for mixed Cr-Al PMs. But for Cr and Cr-AlPMs, the electron accepting capacities are more than that of AlPM. Incorporation of Cr into the AlPM also increased the electron accepting capacity and hence the acidity.

counts the total acidity obtained by temperature programmed desorption of ammonia. Almost all the samples showed a maximum of acid sites in the weak region. As the iron content increases, the total acidity and also the acidity in the strong acid region increase. For Fe-Al$_{1.0}$PM both the total acidity and the number of stronger acid sites are less than Fe-Al$_{0.5}$PM, which is in agreement with the perylene data. However, the magnitude of acidity obtained by TPD method is very much higher than that obtained by perylene adsorption. Perylene measures only the Lewis acidity of the samples and being a large molecule, it may have access only to a smaller amount of acid sites compared to NH$_3$. Besides adsorption on Lewis and Bronsted acid sites, NH$_3$ has the following modes of adsorption also viz., (a) hydrogen bonding to a surface oxygen atom (or to the oxygen of a surface hydroxyl group) and (b) a complete transfer of protons to the NH$_3$ molecules from Bronsted sites to produce adsorbed NH$_4^+$ ions[26]. Ammonia being a small molecule has access to almost all surface sites (both Bronsted and Lewis acid sites) and hence the acidity obtained by TPD method is high.

In contrast to mixed Fe-Al pillared systems, as the chromium content increases the total acidity decreases first (up to 0.5) and for CrAl$_{1.0}$PM, the total acidity increases. This is in an opposite trend compared to the electron accepting capacity values, though the increase in electron accepting capacity is not regular. This discrepancy may be due to the fact that perylene measures only the Lewis acidity and NH$_3$ detects almost all types of acid sites.

*(b) TPD studies*

Figures 3 and 4 show the distribution of acid sites in the weak, medium and strong regions and also

*Catalytic activity*

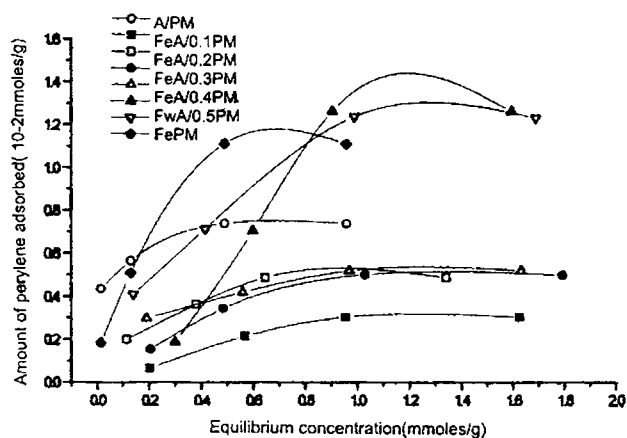The benzoylation activities of different catalysts are depicted in Tables 7 and 8 for comparison. The parent



Fig. 1—Electron accepting properties of mixed Fe-Al pillared montmorillonites determined by perylene adsorption method.
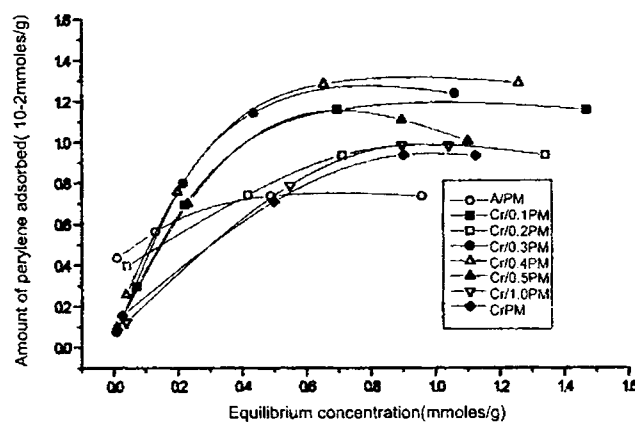


Fig. 2—Electron accepting properties of mixed Cr-Al pillared montmorillonites determined by perylene adsorption method.
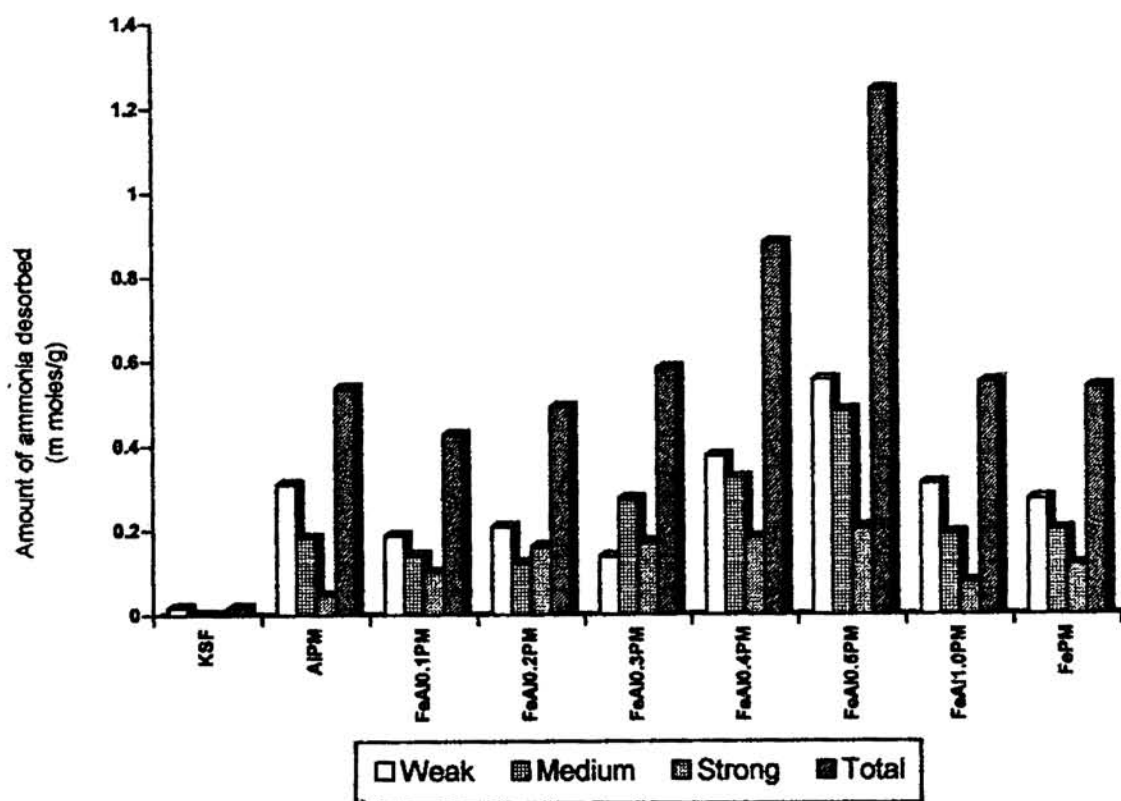
Fig. 3—Acidity distribution among the weak, medium and strong regions in mixed Fe-Al pillared montmorillonites
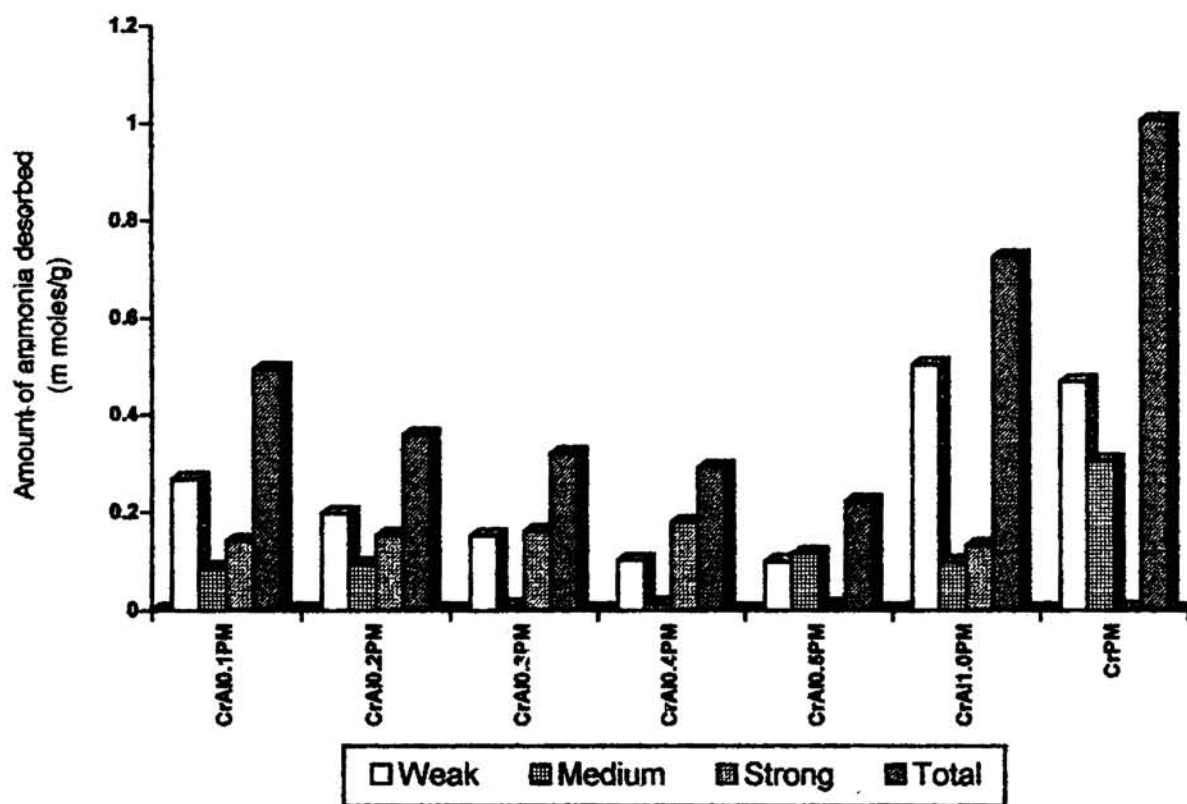


Fig. 4—Acidity distribution among the weak, medium and strong regions in mixed Cr-Al pillared montmorillonites

Table 7—Benzoylation of toluene with mixed Fe-Al pillared clays

| Catalyst | Conversion (%) | Selectivity (%) | |
| --- | --- | --- | --- |
| | | Ortho | Para |
| KSF | Nil | — | — |
| AlPM | 44.58 | 16.01 | 83.99 |
| $FeAl_{0.1}PM$ | 56.95 | 8.03 | 91.96 |
| $FeAl_{0.2}PM$ | 65.43 | 16.33 | 83.66 |
| $FeAl_{0.3}PM$ | 81.31 | 15.81 | 84.19 |
| $FeAl_{0.4}PM$ | 63.22 | 19.94 | 80.05 |
| $FeAl_{0.5}PM$ | 84.34 | 16.26 | 83.74 |
| $FeAl_{1.0}PM$ | 76.65 | 14.98 | 85.02 |
| FePM | 81.82 | 18.00 | 82.00 |

Table 8—Benzoylation of toluene with mixed Cr-Al pillared clays

| Catalyst | Conversion ( %) | Selectivity ( % ) | |
| --- | --- | --- | --- |
| | | Ortho | Para |
| Al PM | 44.58 | 16.01 | 83.99 |
| $CrAl_{0.1}PM$ | 41.14 | 17.48 | 82.52 |
| $CrAl_{0.2}PM$ | 55.32 | 15.38 | 84.62 |
| $CrAl_{0.3}PM$ | 56.38 | 15.52 | 84.48 |
| $CrAl_{0.4}PM$ | 60.26 | 16.44 | 83.55 |
| $CrAl_{0.5}PM$ | 31.16 | 16.99 | 83.01 |
| $CrAl_{1.0}PM$ | 56.46 | 20.19 | 79.81 |
| Cr PM | 29.34 | 0.00 | 100.00 |

montmorillonite displayed poor activity in the reaction under optimized conditions. It is due to very low surface area and the unavailability of stronger acid sites. Iron containing pillared systems showed maximum activity for the benzoylation of toluene compared to other systems. FePM showed 81.82% conversion of benzoyl chloride. AlPM has only a conversion capacity of 44.5%. Among mixed Fe-Al PMs, $Fe-Al_{0.5}PM$ converted benzoyl chloride to the maximum extent. This is explained by the fact that the total acidity as well as the number of strong acid sites increases as the Fe/Al ratio increases and is maximum for $Fe-Al_{0.5}PM$. Lewis acidity determined by perylene adsorption was also maximum in the case of Fe/Al ratio of 0.5. $Fe-Al_{0.3}$ PM showed more activity than $Fe-Al_{0.2}PM$ and $Fe-Al_{0.4}PM$, though they displayed similar perylene adsorption data. Also the total acidity of $Fe\ Al_{0.4}PM$ is greater than those of the other two. This suggests that some other factors also have role in the activity. It is reported that a combination of Bronsted acidity and Lewis acidity is responsible for benzoylation reaction[27]. The catalytic activity of Cr-Al PMs is comparatively less than that

of iron systems due to the lesser number of strong acid sites. CrPM possessed very less number of strong acid sites and about 29.3 % conversion is obtained. Among Cr-AlPMs, $Cr-Al_{0.4}PM$ showed maximum conversion. Though the total acidity of Cr-Al systems decreases up to a Cr/Al ratio 0.4, the acidity in the strong acid region increases up to that ratio. Lewis acidity measurements also showed a maximum Lewis acidity for $CrAl_{0.4}PM$.

## Conclusions

The dramatic increase form $6 m^2/g$ to a maximum of $198\ m^2/g$ confirms that efficient pillaring has taken place. The present study ensures perylene adsorption method as a promising one to get an insight of the electron accepting capacities of the acidic catalysts. Incorporation of a second metal into a single oxide pillared system, changed the properties of the samples and a mixed pillared system of Fe-Al and Cr-Al viz., $Fe-Al_{0.5}PM$ and $Cr-Al_{0.4}PM$ respectively are found to be efficient than the single oxide pillared systems. The present study also reveals that benzoylation activity depends on the strong acid sites and may be a combination of Bronsted and Lewis acidity of the samples. Iron containing systems possessed more active sites compared to other systems.

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