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# Surface Acidity-Cracking Activity Correlation in Chromium Pillared Clays

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Chromium pillared montmorillonite and vermiculite catalysts have been prepared by intercalation with hydrolyzed metal ion solution. Pillaring solutions with different chromium concentrations were prepared by varying the base to chromium ratio. The catalysts were characterized by nitrogen adsorption, XRD, and IR studies. The nature of the acid sites was characterized by means of IR spectra data on pyridine adsorbed chromium pillared catalysts. The acidity of the samples was determined by butylamine titration. DSC has been used in the present study to probe the nature of the surface acidity, its heterogeneity, acid strength, and density of acidic sites. Cumene cracking was carried out as a test reaction of Brønsted acidity. Both the density and strength of Brønsted acid sites were found to influence the cracking activity.

Pillared clays are generally prepared by exchanging polymeric hydroxometal complexes (polyoxo cations) with the exchangeable cations that exist between the clay layers. These metal complexes undergo dehydration and dehydroxylation when calcined and they form thermally stable polyoxometal species which act as pillars between the layers. The oxide pillars, thus formed prop open the clay layers, creating a two-dimensional pore structure with high surface area.[1)] Pillared clays based on Al, Zr, Fe, Cr, and Ni pillaring agents have been reported.[2—6)] Pillared clays have been studied for a variety of acid catalyzed reactions.[7—9)] In the present work, chromium pillared clay catalysts have been prepared by intercalating montmorillonite and vermiculite with different chromium concentrations. Cumene cracking was chosen as a model reaction to correlate the surface acidic characteristics of chromium pillared clays with their cracking activity.

## Experimental

**Materials:** Montmorillonite (Fluka) and vermiculite (Tamil Nadu Minerals Ltd.) clays were used in the present study. Other chemicals used such as sodium chloride, sodium carbonate, cumene, and chromium chloride were of AR BDH/CDH/Fluka grade.

**Preparation of Chromium Pillared Clay Catalysts:** The chromium pillared montmorillonite and vermiculite clay catalysts were prepared by adopting the procedure given in the literature.[10)] Initially the preparation of polyoxo metal complexes for the pillaring of clays was carried out by hydrolysing the metal ion solution using solid sodium carbonate as the source of base. Solid sodium carbonate was added to a solution of chromium(III) chloride (0.1 M, 1 M=1 mol dm$^{-3}$) at room temperature with constant stirring. The solution was allowed to age at 95 °C for 36 hours. Pillaring solutions were prepared by varying the base to chromium ratio ($n$) over the range 0.25 to 1.0 mmol $CO_3^{2-}$/mmol $Cr^{3+}$. Extensive precipitation of chromium(III) hydroxide occurred at "$n$" values greater than 1. So the corresponding pillaring solutions could not be prepared. A suspension of the sodium form of clay was added in the ratio of 50 mmol Cr/meq clay to the pillaring chromium solution with constant stirring. The stirring was continued for 2 h. The product mixture was filtered. The solid mass was washed repeatedly with distilled water and air dried at room temperature. The dried sample was calcined at 500 °C for 3 h in nitrogen atmosphere. The catalysts prepared with different chromium content in the present study are given in the Table 1.

**Characterization of Chromium Pillared Clays:** Chromium content of the catalysts prepared was determined spectrophotometrically.[11)] Surface area of the samples was determined by nitrogen adsorption using Micromeritics Pulse Chemisorb 2700. The intercalation of the clays was confirmed by XRD and infrared spectra. The nature of the acid sites was characterized on the basis of infrared spectral data on pyridine adsorbed chromium pillared catalysts. The total acidity of the samples was determined by butylamine titration. Differential scanning calorimetry with a nullifying technique[12)] has been used to determine the nature of acidic sites, the acid strength as well as the density of the acidic sites.

**Cracking Activity:** The cracking activity of the catalyst samples was determined in vapor phase in a fixed bed flow reactor packed with about 0.2 g of the catalyst. Temperature and contact time were varied to study their influence on the cracking activity. The flow rate of cumene was controlled with the help of an infusion pump and the product stream from the reactor was condensed and subjected to gas chromatographic analysis.

## Results and Discussion

Intercalation of the clays with chromium pillaring solutions prepared with different "$n$" values resulted in pillared clays with different chromium loading. The chromium content of the various samples are indicated by numerical subscripts in the sample codes. The surface area of the catalysts as determined by nitrogen adsorption technique was found to increase linearly with increasing chromium content in the case of montmorillonite based catalysts. There was no appreciable enhancement in the surface area in the case of vermiculite based catalysts and the values are given in Table 1. The X-ray diffractogram indicated the enhancement of $d_{001}$ spacing from 9.4 Å of raw clay to 15.68 Å for a representative chromium pillared montmorillonite clay ($PM{-}Cr_{2.84}$) catalyst. The presence of two types of

Table 1. Surface Area and Acidity Determination of Chromium Pillared Clay Catalysts

| Catalysts[a)] | Surface area ($m^2\,g^{-1}$) | Acidity determination | | | |
|---|---|---|---|---|---|
| | | Titrimetry ($mmol\,g^{-1}$ butylamine) | DSC data | | |
| | | | Peak temp (°C) | $\Delta H_{exo}$ ($J\,g^{-1}$) | Assignment[b)] |
| M–Cr$_{0}$ | 20 | 0.31 | — | — | — |
| PM–Cr$_{1.34}$ | 81 | 0.59 | 105.0 | 54 | WA |
| | | | 270.0 | 3 | LA |
| | | | 422.0 | 132 | BA |
| PM–Cr$_{2.84}$ | 144 | 0.65 | 128.8 | 111 | WA |
| | | | 265.8 | — | LA |
| | | | 395.0 | 159 | BA |
| PM–Cr$_{3.03}$ | 166 | 0.66 | 125.7 | 32 | WA |
| | | | 262.4 | — | LA |
| | | | 390.4 | 257 | BA |
| PM–Cr$_{4.20}$ | 186 | 0.59 | 132.0 | 28 | WA |
| | | | 380.4 | 415 | BA |
| PM–Cr$_{6.29}$ | 260 | 0.50 | 104.0 | 75 | WA |
| | | | 380.8 | 436 | BA |
| V–Cr$_{0}$ | 4 | 0.05 | — | — | — |
| PV–Cr$_{1.02}$ | 14 | 0.36 | — | — | — |
| PV–Cr$_{1.45}$ | 22 | 0.43 | 122.0 | 17 | WA |
| | | | 254.7 | 7 | LA |
| | | | 425.6 | 109 | BA |

a) PM and PV indicates chromium pillared montmorillonite and vermiculite. Numerical subscripts in the sample code indicate the chromium content (wt%). b) WA, LA, and BA indicate pyridine desorbed from Weak acid sites, Lewis acid sites, and Brønsted acid sties, respectively.

hydroxyl groups, namely the surface OH groups and the OH groups on the pillars have been identified by IR absorption bands in the 3700—3500 $cm^{-1}$ region. The IR spectra of pyridine adsorbed chromium pillared clay catalysts showed the presence of three types of acid sites. The presence of Lewis, Brønsted and weak acidic sites was indicated by strong IR absorption bands of coordinated pyridine at 1445, 1491, and 1642 $cm^{-1}$ (Lewis acid sites); of pyridinium ion at 1631, 1590, and 1550 $cm^{-1}$ (Brønsted acid sites), and of hydrogen bonded/physisorbed pyridine at 1443 and 1488 $cm^{-1}$ (weak acid sites) respectively.[13)] The undissociated surface hydroxy groups incapable of coordinating with pyridine or forming a pyridinium ion function as weak acid sites. The pyridine molecules are probably held by these weak acid sites through hydrogen bonding. IR spectra recorded for a representative sample PM–Cr$_{1.34}$ is shown in Fig. 1. The acidity determined by butylamine titration indicated that the overall acidity has been varied to different extents due to intercalation with varying base to metal ratio. In the case of montmorillonite based catalysts the overall acidity gradually increased upto a chromium content of 3.03% and declined with further increase in metal content. The DSC thermograms of the chromium pillared catalyst samples showed three distinct peaks, clearly indicating the heterogeneity of the surface acidity. The peak temperatures were found to be in the range of (i) 105—135 °C, (ii) 260—270 °C, (iii) 380—422 °C. The desorption peak in the higher temperature range has been attributed to the desorption of pyridine from Brønsted acid sites. The desorption peak in the intermediate temperature indicated the desorption of pyridine from Lewis acid sites. The desorption peak in the lower temperature range has been attributed to the desorption of pyridine from weak acid sites. A representative DSC thermogram is shown in Fig. 2.

**Cracking Activity of Chromium Pillared Clay Catalysts:** Cracking of cumene was quantitatively studied by varying the reaction temperature and contact time for the chromium pillared clay catalysts prepared with different concentrations of chromium. A fresh batch of catalysts was used for each experiment. Product analysis showed that the main product was benzene. A small percentage of other products, viz. cyclohexene and ethylbenzene were also obtained.

**Effect of Temperature:** The effect of temperature on percentage conversion of cumene at a fixed contact time was investigated for the chromium pillared clay catalysts in the temperature range of 573—773 K. The

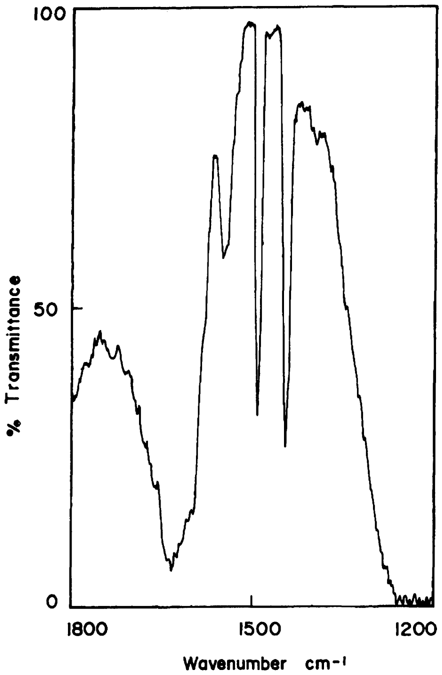

Fig. 1. IR spectrum of pyridine adsorbed on PM–$Cr_{1.34}$ using self supporting wafer.

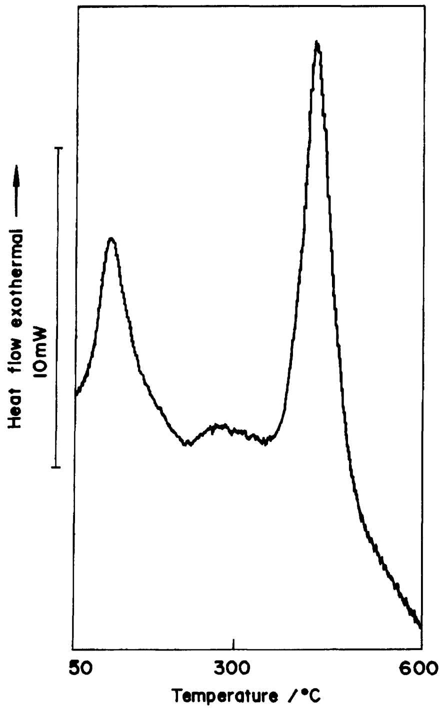

Fig. 2. DSC thermogram of pyridine desorption from PM–$Cr_{1.34}$.

percentage conversion of cumene was found to increase with increasing reaction temperature. Cracking of cumene on chromium pillared vermiculites occur at higher temperatures compared to chromium pillared montmorillonite. The product selectivity towards benzene was found to be higher in the case of chromium pillared montmorillonites. Beyond 773 K the product selectivity towards benzene was found to be less.

**Effect of Chromium Concentration:** The effect of chromium concentration of chromium pillared montmorillonite and vermiculite catalysts on the cracking activity was studied at a fixed contact time ($W/F$=27.85 g h/g mol) and temperature (723 K). In the case of chromium pillared montmorillonite catalysts PM–$Cr_{2.84}$ showed higher cracking activity whereas PM–$Cr_{4.20}$ showed higher selectivity towards benzene (Table 2). In the case of chromium pillared vermiculites, PV–$Cr_{1.45}$ showed higher cracking activity as well as higher selectivity towards benzene.

**Effect of Time on Stream:** The effect of time on stream on cumene cracking was studied for the chromium pillared clay catalysts by collecting the products at regular time intervals. Due to coke formation the cracking activity was found to decrease with time and the catalysts were active upto 3 h.

**Kinetic Studies:** The kinetics of the cumene cracking reaction was studied for the sample PM–$Cr_{2.84}$ by varying the contact time ($W/F$) from 13.92 to 27.85 g h/g mol and temperature of the catalyst bed was varied in the range of 658 to 708 K. Experimental data were analyzed on the basis of the integral method[14] by using the equation

$$-x' - 2\ln(1 - x') = kP_{\mathrm{T}}/RT(W/F), \tag{1}$$

where $x'$ is the fractional conversion, $k$ is the rate constant, $P_{\mathrm{T}}$ is the total pressure, $R$ is the gas constant, and $T$ is the temperature.

The plots of $-x' - 2\ \ln\ (1-x')$ vs. $W/F$ (Fig. 3) at different temperatures were straight lines and passed through the origin indicating the reaction to be first order with respect to the concentration of cumene. From the slope of the Arrhenius plot of $\log k$ vs. $1/T$ the activation energy $E_a$ (95.7±1 kJ mol$^{-1}$) and the frequency factor $A$ ($7.282\times10^6$) were calculated.

**Cracking Activity and Surface Acidity-Correlation:** A comparison of acidity values among the chromium montmorillonites (Table 1) showed that the sample PM–$Cr_{3.03}$ has higher acidity as determined by titrimetry. PM–$Cr_{2.84}$ exhibits slightly lower acidity values than that of PM–$Cr_{3.03}$. Both PM–$Cr_{2.84}$ and PM–$Cr_{3.03}$ showed higher cracking activity. Thus a direct correlation between the cracking activity and surface acidity was established. It is well known that Brønsted acidity is responsible for cracking activity of acid catalysts. The density of Brønsted acidity among the chromium pillared clays (as indicated by $\Delta H$ values from DSC thermogram), and the strength of the Brønsted acid sites (as indicated by peak temperature of the DSC curve) followed opposite trends as a function of chromium weight percentage. The density of Brønsted acidity increased with increasing chromium content but the strength of Brønsted acid sites decreased with increasing chromium content. The variation of density

Table 2. Cracking Activity of Chromium Pillared Clay Catalysts

| Catalysts | % Product distribution | | | Conversion of cumene | Selectivity towards benzene |
|---|---|---|---|---|---|
| | Cyclohexene | Benzene | Others | % | % |
| M–Cr$_{0}$ | — | — | 3.5 | 3.5 | — |
| PM–Cr$_{1.34}$ | 5.0 | 11.1 | 2.5 | 18.9 | 58.7 |
| PM–Cr$_{2.84}$ | 14.6 | 11.2 | 3.9 | 30.5 | 36.7 |
| PM–Cr$_{3.03}$ | 12.8 | 10.9 | 3.2 | 28.3 | 38.5 |
| PM–Cr$_{4.20}$ | 2.0 | 16.6 | 3.2 | 21.7 | 76.5 |
| PM–Cr$_{6.29}$ | 1.0 | 6.1 | 2.6 | 9.4 | 64.8 |
| V–Cr$_{0}$ | — | — | 1.5 | 1.5 | — |
| PV–Cr$_{1.02}$ | — | 6.0 | 3.0 | 10.0 | 60.0 |
| PV–Cr$_{1.45}$ | — | 10.0 | 2.0 | 13.0 | 76.9 |

Reactions conditions: $W=0.2$ g, $W/F=27.85$ gh/gmol, $T=723$ K. Data taken after 0.5 h time on stream.

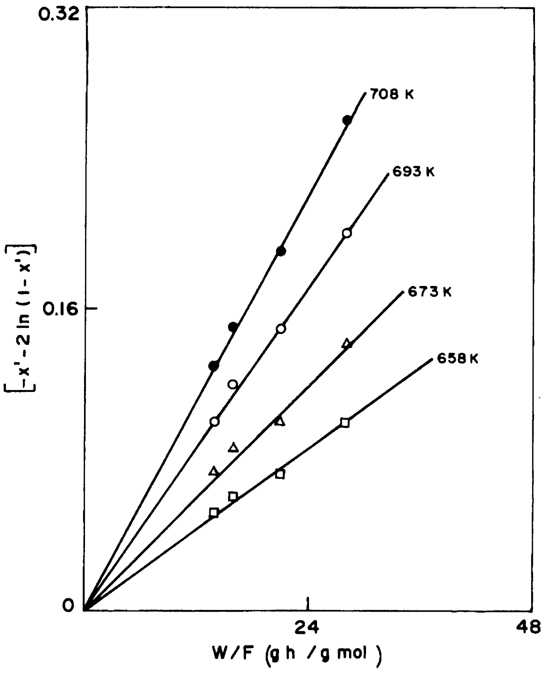

Fig. 3. Effect of contact time on cracking of cumene on PM–Cr$_{2.84}$. Plot of $[-x'-2\ \ln\ (1-x')]$ vs. $W/F$.

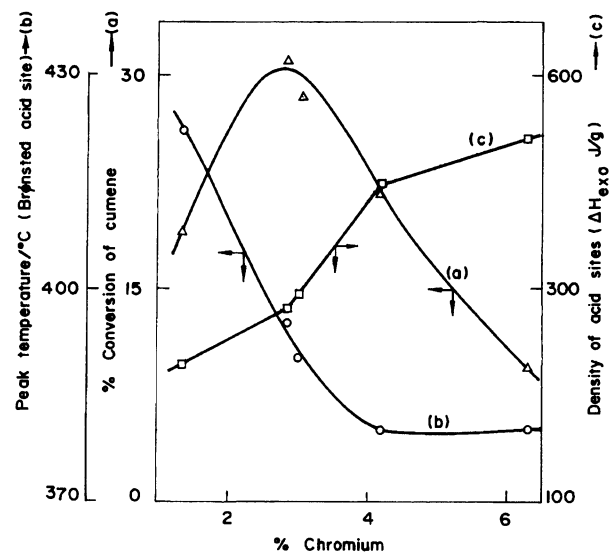

Fig. 4. Correlation between acidic characteristics and cracking activity on chromium pillared montmorillonites.

of acid sites, the corresponding peak temperature as a function of weight percentage of chromium along with percentage conversion of cumene are shown in Fig. 4. A direct correlation of the cracking activity independently either with density or strength of Brønsted acid sites was not possible. Thus the density as well as the strength of Brønsted acid sites influence the cracking activity.

## Conclusions

Chromium pillared montmorillonite and vermiculite clay catalysts with different chromium concentrations can be prepared by varying the base to chromium ratio. The surface acidity of the catalysts varied with chromium content. Pillaring has enhanced Brønsted acid density only and not that of Lewis acid sites. The cracking activity was found to be dependent on the acidic characteristics, particularly on both the density and strength of Brønsted acid sites.

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