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Cracking Selectivity of a Delaminated Clay Catalyst

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Gas oil cracking selectivity is reported for a delaminated clay catalyst formed by the reaction of polyoxoaluminum cations with Laponite, a synthetic small particle hectorite. The C_5–C_{12} gasoline yields obtained with the delaminated clay more nearly approximate the selectivity of a commercial zeolite-promoted FCC catalyst than an amorphous aluminosilicate catalyst (AAA-alumina). In addition, the delaminated clay affords higher yields of light cycle gas oil and lower yields of slurry oil than the zeolite-promoted catalyst. This latter property is found also for clays which are pillared by polyoxoaluminum cations. The zeolite-like cracking properties and similarities to conventional pillared clays-suggest that some two-dimensional zeolitic character is retained by the delaminated clay, despite the absence of discrete 001 X-ray reflections and the presence of an appreciable macroporous component. The zeolite-like cracking selectivity, as well as the amorphous oxide-like macroporosity, is consistent with a previously proposed house-of-cards structure for the delaminated clay.

INTRODUCTION

Clays have played a historically important role in the petroleum refining industry. For instance, when the first fixed-bed Houdry process came on stream in 1936, it made use of a clay-derived catalyst (*1*). Clays continued to be important in the development of fluidized catalytic cracking (FCC) processes (*2*), but by the end of World War II they began being replaced by synthetic aluminosilicates and, eventually, by zeolites.

Recently, there has been a resurgence of research on clays as cracking catalysts (*3–5*). This renewed interest is stimulated in part by the realization that montmorillonite and related smectite clays can imbibe robust cations which transforms them into "pillared" or two-dimensional expanded structures with zeolite-like properties (*6*). Clays pillared by polyoxocations, for example, can catalyze the conversion of gas oil fractions to transportation fluids (*3, 5*), the dehydration of alcohols to hydrocarbons (*7, 8*), and other useful reactions (*9*).

Recently, Pinnavaia and his co-workers (*10, 11*) discovered that the same polyoxocations used to pillar smectite clays can also be used to delaminate clays. The delamination phenomenon is facilitated by clay platelets of small size and lath-shape morphology. These particle properties promote platelet association through edge to face interactions and the formation of a house-of-cards structure. Consequently, these new delaminated clays exhibit a macroporous structure which is not present in well-ordered pillared clays.

The lack of long-range layer stacking in a delaminated clay is indicated by the absence of distinct 001 X-ray reflections (*11*). The absence of such reflections, however, does not preclude the possibility of short-range layer ordering over a few clay sheets. If short-range layer ordering does occur, it should be reflected in zeolite-like catalytic selectivity for the delaminated clay. The present paper examines the gas oil cracking selectivity of a delaminated clay formed by the reaction of polyoxoaluminum cations with Laponite, a synthetic small particle

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hectorite. The results are compared with those obtained for a commercial zeolite-promoted FCC catalyst and an amorphous synthetic silica-alumina catalyst.

EXPERIMENTAL

Delaminated clay catalyst. The delaminated clay catalyst used in this work was prepared by reaction of a synthetic hectorite, Laponite (Laporte Industries, Ltd.), and an aluminum chlorohydrate solution, Chlorhydrol (Reheis Chemical Co.), according to previously described procedures (*11*). Elemental analysis indicated an empirical unit cell composition of $(Al(OH)_{2.95})_{5.00}[Mg_{5.75}Li_{0.25}](Si_{8.00})O_{20}(OH)_4$. The concentrations of Na, K, Ca, and Fe oxides as contaminants were <0.05 wt%. The N_2 BET surface area after activation at 350°C was 381 m^2/g. As reported previously (*11*), X-ray diffraction patterns of film samples indicated the absence of distinct 00l reflections. This result is consistent with the absence of long-range layer stacking. Mercury porosimetry (60,000 psi) indicated that 63% of the total Hg pore volume (0.174 cc/g) arises from pores with diameter >1000 Å. The apparent surface area deduced from porosimetry was 52.3 m^2/g.

Catalyst testing. Catalyst evaluation was performed using a microactivity test (MAT) similar to the one described by Ciapetta and Anderson (*12*), except that the feed was injected by syringe and the liquid product recovery was established gravimetrically. The conversions were on a vol% fresh feed (FF) basis and were defined as $[V_f - V_p/V_f] \times 100$, where V_f is the volume of feed and V_p is the volume of product with bp > 204°C. The following reaction parameters were used: weight-hourly space velocity, 15; contact time 80 sec; temperature 515°C; catalyst-to-oil ratio, 2.5 (w/w). The feed stock (Cincinnati Gas Oil Co.) was a gas oil with a 260–426°C boiling point range. The slurry oil (bp 343–426°C), light cycle gas oil (bp 221–343°C), and gasoline content of the gas oil was 74.3, 23.0, and 2.7%, respectively. The same gas oil was used previously to evaluate the cracking activity of a montmorillonite pillared by aluminum chlorohydrate (*5*). The deactivation of the delaminated clay catalyst was accomplished by passing dry air or a mixture of 95% steam–5% N_2 over the catalyst for 6 h at temperatures in the 300–600°C range. The commercial catalysts used as references were treated with steam at higher temperatures or for longer periods of time to obtain the desired conversion level.

RESULTS AND DISCUSSION

The activity of our delaminated clay catalyst for gas oil cracking is similar to the activity of an amorphous AAA-alumina catalyst (78% SiO_2, 22% Al_2O_3). However, the selectivity of the delaminated clay catalyst more nearly resembles the selectivity of a typical commercial zeolite-promoted FCC catalyst. The zeolite-like activity is indicated by the gasoline yields for conversions in the 54 to 67% range. As shown in Fig. 1, the C_5–C_{12} yields for the delaminated catalyst are in the same range as the commercial FCC catalyst and are significantly larger than those obtained with amorphous AAA-alumina.

As shown in Fig. 2A, the yields of light cycle gas oil (LCGO) obtained with the delaminated clay are higher than those obtained with either the AAA-alumina or the commercial FCC catalyst. The enhanced LCGO yields are accompanied by low slurry oil (SO) yields, as illustrated by the

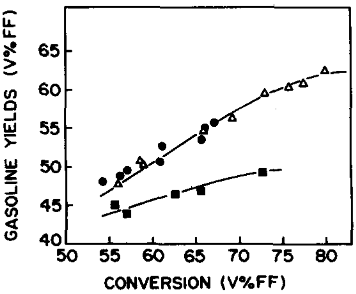

FIG. 1. Gasoline (C_5–C_{12}) yields obtained with delaminated clay (●), AAA-alumina (■), and zeolite-promoted FCC (△) catalysts.

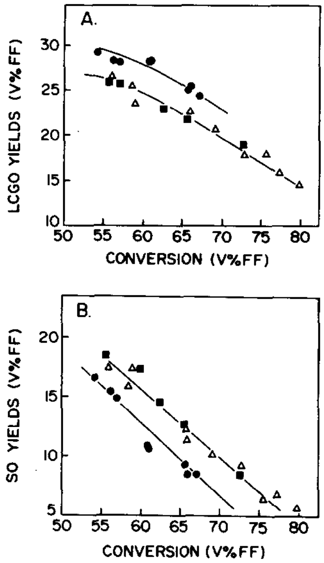

FIG. 2. (A) Light cycle gas oil (LCGO) yields and (B) slurry oil (SO) yields obtained with delaminated clay (●), AAA-alumina (■), and zeolite-promoted FCC (△) catalyst.

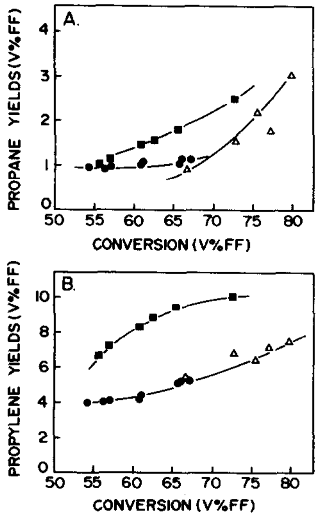

FIG. 3. (A) Propane and (B) propylene yields obtained with delaminated clay (●), AAA-alumina (■), and zeolite-promoted FCC (△) catalyst.

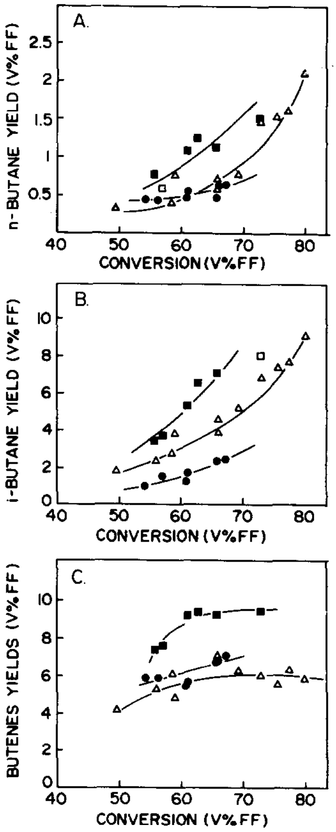

FIG. 4. (A) n-Butane, (B) i-butane, and (C) butenes yields obtained with delaminated clay (●), AAA-alumina (■), and zeolite-promoted FCC (△) catalysts.

results presented in Fig. 2B. Thus, the delaminated clay converts more of the heavier gas oil components to the more desirable LCGO fraction. The selectivity of the delaminated clay toward gasoline and LCGO occurs without increasing the overall yield of light gases. This result is indicated by the yields of propane and propylene in Fig. 3, along with the yields of n-butane, i-butane and butenes in Fig. 4.

The hydrogen and coke yields provided in Figs. 5 and 6 are significantly larger than

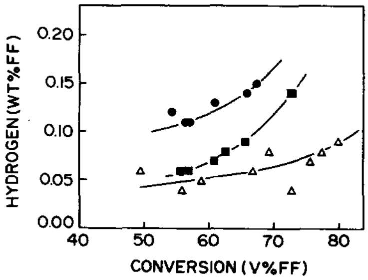

FIG. 5. H_2 yields obtained with delaminated clay (●), AAA-alumina (■), and zeolite-promoted FCC (△) catalysts.

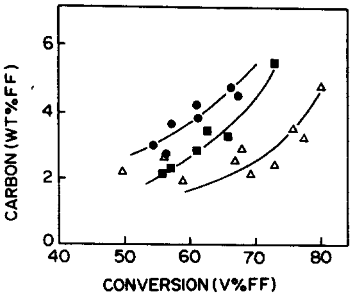

FIG. 6. Carbon yields obtained with delaminated clay (●), AAA-alumina (■), and zeolite-promoted FCC (△) catalysts.

is typical for either a zeolitic or amorphous catalyst. The tendency for the delaminated clay to form coke may be related to the macroporosity of this catalyst. Certainly, aromatic molecules can readily adsorb in the macroporous structure. The interactions of the adsorbed aromatics with Lewis acid sites on the dehydroxylated oxocations could facilitate polycondensation of the aromatic centers and the formation of coke and hydrogen.

The selectivity described above for the delaminated clay catalyst is very similar to the selectivity exhibited by a conventional pillared clay for the cracking of the same gas oil sample under analogous reaction conditions (*5*). The pillared clay gave a somewhat lower gasoline yield and somewhat higher light gas and carbon yields than the delaminated clay, but the relative LCGO and SO yields are very similar to those for the delaminated clay. The tendency of the pillared clay to give less gasoline, more light gas, and more coke than the delaminated clay may be related in part to the iron contents of the two catalyst. The parent clay used to prepare the previously reported pillared catalyst (*5*) was a natural montmorillonite. These natural clays typically contain 1–4 wt% Fe_2O_3 with the iron being present both as an oxide impurity and as structural iron. In contrast, our delaminated clay is prepared from a synthetic smectite which contains only trace amounts ($<$0.04%) of iron oxide (*11*). Iron can facilitate the cracking of heavier hydrocarbons to light gases and promote coke formation (*13*).

The similar cracking selectivities for delaminated and pillared clay catalysts suggest that the delaminated clay possess significant two-dimensional zeolitic character. Zeolite-like catalytic properties persist for the delaminated clay despite the presence of macroporosity and the lack of X-ray evidence for long-range layer stacking. The previously proposed house-of-cards model (*11*) for a delaminated clay is consistent with the presence of zeolite-like microporosity, as well as macroporosity. The house-of-cards model is shown in Fig. 7. Included in the figure is a model for the structure of a well-ordered pillared clay.

In the delaminated clay model shown in Fig. 7A, the extensive edge to face interac-

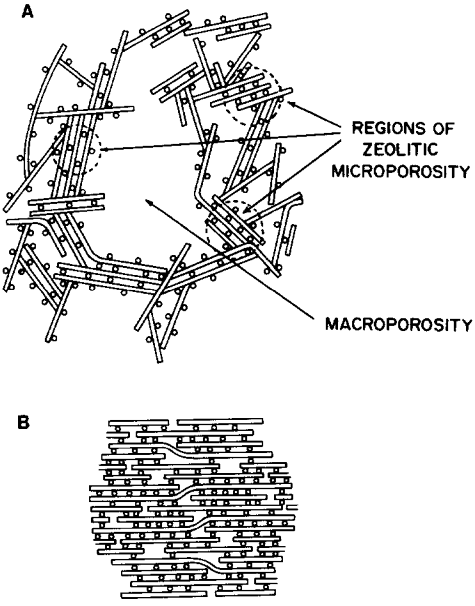

FIG. 7. (A) House-of-cards structure for a delaminated clay catalyst. Layer stacking (face to face) is short range, occuring over 2–3 silicate layers. Short-range layer stacking generates zeolite-like microporosity, whereas edge to face association of the layers generates macroporosity. (B) The long-range layer stacking in a well-ordered pillared clay. The long-range ordering of layers and the regular spacing of intercalated oxocations results almost exclusively in zeolite-like microporosity.

tions lead to the formation of macropores. In addition, some face to face layer stacking takes place, in accord with the zeolite-like cracking selectivity found in the present work. However, the layer stacking is short-range, occurring only over a few (2 to 3) layers (40–60 Å), thus accounting for the absence of discrete 001 X-ray reflections. It should be noted, however, that the intercalated oxocations in these short-range stacked layers may not be as regularly spaced as in a well-ordered pillared clay. Evidence supporting a distribution of micropores in a delaminated clay has been provided previously by Pinnavaia and coworkers (*11*) on the basis of physical adsorption data for molecules of different kinetic diameters.

In contrast to the short-range layer ordering which occurs for a delaminated clay, the layer stacking in a well-ordered pillared clay occurs over a much longer range (cf. Fig. 7B). Also, the spacing of pillars is quite regular. Thus, a pillared clay exhibits several 001 X-ray reflections, along with well-defined molecular sieving properties. However, well-ordered pillared clays lack the macroporosity and facile diffusion properties (*11*) of a delaminated clay.

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