

Catalytic Reactions by Thermally Activated, Synthetic, Anionic Clay Minerals

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The thermal decomposition of a number of anionic clay minerals belonging to the pyroaurite-sjogrenite group, such as hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3^-) \cdot 4\text{H}_2\text{O}$), results in a product (approximately $\text{Mg}_6\text{Al}_2\text{O}_8(\text{OH})_2$) which is a fairly strong base ($\text{p}K_a \leq 35$) and a useful catalyst for vapor-phase aldol condensations. Replacement of Mg by Fe, Co, Ni, and Zn, and/or replacement of Al by Fe and Cr also results in isomorphous double hydroxides which, on heat treatment, are catalytically active. A rational method of synthesizing these materials having controlled surface areas has been devised. The effect of the thermal decomposition temperature, Mg/Al ratio, isomorphous metal cation substitution, and interstitial anion nature on the rate and efficiency of acetone oligomerization has been examined. These materials will also catalyze H-D exchange of acetone and toluene but not of *n*-propylbenzene or cyclohexane (300°C, LHSV ~1). They are relatively poor catalysts for olefin isomerization as well as aromatization of 1,4-cyclohexadiene and limonene.

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INTRODUCTION

Heterogeneous catalysts which have a pronounced but controlled basic character and are also substantially devoid of acidic sites are relatively rare. Certain synthetic, anionic clay minerals, on heating, yield materials which function effectively as catalysts for base-catalyzed reactions. This report discusses the synthesis of a class of anionic clays which, after heat treatment, results in excellent vapor-phase aldol catalysts. Additionally, a number of peripheral, base-catalyzed reactions involving these materials have been explored.

Clay minerals (1) are composed of infinite layers of metal or nonmetal oxides and hydroxides stacked on top of each other. In the case of ubiquitous cationic clays, interlayer cations (Na^+ , K^+ , Ca^+ , etc.) charge-neutralize the negatively charged sheets. The far less common anionic clays (2, 3) have positively charged metal oxide/hydroxide layers with anions located interstitially. Many of these are based on double

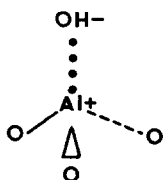
hydroxides¹ of the main group (Mg, Zn, Al) and the transition metal (Fe, Co, Ni, Cr) hydroxides. The structure of these materials is very similar to that of brucite ($\text{Mg}(\text{OH})_2$). Here, the magnesium cation is octahedrally surrounded by hydroxyl groups; the resulting octahedra share edges to form infinite sheets (3). When some of the magnesium in this lattice is isomorphously replaced by a higher charged cation, e.g., Al^{3+} , then this Mg^{2+} - Al^{3+} -OH layer gains positive charge. An appropriate number of interstitial anions, of almost any kind but most frequently carbonate, render this arrangement electrically neutral. The particular double hydroxides of interest here belong to the Mg^{2+} - Al^{3+} series (hydrotalcite or manasite its polytype (4, 5)). Hydrotalcite has the ideal unit cell formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3^-) \cdot 4\text{H}_2\text{O}$; the ratio of Mg/Al can be quite variable (1.7-4, (6)) in

¹ The double hydroxides of interest here are collectively referred to as the pyroaurite-sjogrenite group of minerals with the idealized, formal unit cell composition $M_6^+M_2^{3+}(\text{OH})_{16}(\text{A}^-)_2 \cdot n\text{H}_2\text{O}$ (2).

synthetic samples. By synthesis, materials with Mg replaced by Zn, Fe, Co, Ni, Cu, and Al replaced by Cr and Fe have been prepared. The anion nature is widely variable by synthesis (3, 6), ion exchange (7), or careful neutralization (8) of the carbonate.

The changes which take place on heating hydrotalcite have been reported (9, 10). Below 200°C, only the interstitial water is lost; with further heating to 450–500°C dehydroxylation is complete and the carbonate is lost as carbon dioxide. Eventually, this leaves a residue which analyzes approximately as $Mg_6Al_2O_8(OH)_2$. This process is reversible, provided the heating temperature does not exceed 550–600°C. This heating to 450–500°C results (6, 10) in a modest increase in the surface area from about 120 to 200 m^2/g (BET/ N_2), an increase in the pore volume from about 0.6 to 1.05 cm^3/g (Hg intrusion) and a change in the X-ray powder pattern from that of hydrotalcite to a poorly crystalline magnesium oxide. The morphology of the crystal itself does not change. The gases exit the crystal, not by exfoliation as could be expected, but via craters in the surface and subsurface pores in the metal oxide sheets.

Prior work (6) on this thermal decomposition of hydrotalcite indicated that there were numerous anionic centers present in the product (~ 0.8 meq/g) and that these centers had variable pK_b 's. From the spectroscopic (A1-27-NMR-MAS and XPS (Auger)) data (10), it would appear that the hydroxyls were located at the apices of the tetrahedral aluminum atoms, which are



probably the basic centers detected by the titration techniques (6). Such heated hydrotalcites have already been shown to be catalytically active for the polymerization of

β -propiolactone (11) and propylene oxide (12). It would appear reasonable that similar, base-catalyzed reactions such as aldol condensations (13), would respond to catalysis by these materials. This report deals with a description of the effect of catalyst modifications on the course and rate of the oligomerization of, principally, acetone. The chemistry of this reaction has been elucidated in some detail by pulse reactor (14) and C-13 NMR techniques (15).

EXPERIMENTAL

Hydrotalcite and related materials used here were prepared by a standard aqueous precipitation and heat crystallization procedure (16). It is important to note that the time and temperature of the crystallization step determines the crystal morphology and, in particular, the catalytically important surface area. Thus, at 65°C/18 hr fine platelets ($\sim 0.5 \mu m$) of about 120 m^2/g are produced, while at 200°C/18 hr hexagonal crystals ($\sim 1-2 \mu m$) with only about 12 m^2/g surface area results (BET/ N_2). The former, low-temperature-crystallized, high-surface-area materials, are the catalytically effective materials.

Preparation of Mg-Al- CO_3 hydrotalcite. A solution of 256 g $Mg(NO_3)_2 \cdot 6H_2O$ (1.00 mole) and 187.5 g $Al(NO_3)_3 \cdot 9H_2O$ (0.50 mole) in 700 ml distilled water was added to a solution of 280 g, 50% aq. NaOH (3.50 mole), 100 g Na_2CO_3 (anhydr., 0.943 mole) in 1000 ml distilled water. This addition was carried out in a 3-liter flask equipped with a mechanical stirrer, a dropping funnel, thermometer, and cooling bath. The addition took about 4 hr and was carried out with vigorous agitation. The temperature was at or below 35°C. Following the addition, which resulted in a heavy slurry, the flask contents were heated at $65 \pm 5^\circ C$ for about 18 hr with good mixing. This latter step induces the substantially amorphous precipitate to crystallize. Following the heating period, the slurry was cooled to room temperature, filtered, and washed until the sodium contents of the resulting solid was

below 0.1% (dry basis). The solid was then dried (125°C/vacuum/18 hr) resulting in 100–120 g of a white powder. The X-ray powder pattern of this white powder corresponds to that of hydrotalcite (17); the peaks are relatively broad due to the small crystal size. Anal. found: ash, 57.39%; Mg, 35.34%; Al, 17.72%; Na, 0.006%; N, 0.012%; C, 2.50%. Calculated for $\text{Mg}_6\text{Al}_{2.28}(\text{OH})_{16.56}(\text{CO}_3^{2-})_{1.14} \cdot 6\text{H}_2\text{O}$: ash, 58.38%; Mg, 38.51%; Al, 16.26%; C, 2.11% (Mg and Al on ashed basis).

This procedure is adaptable to variations in the Mg/Al ratio, and cation substitution. The presence of the sodium carbonate materially enhances the rate of filtration: the absence of carbonate results in a finely divided precipitate which is exceptionally difficult to filter. The X-ray powder patterns of these precipitates are those of more-or-less diffuse hydrotalcite (17). The crystal size and perfection determine the powder pattern's sharpness.

Preparation of Cr^{3+} - Zn^{2+} hydrotalcite. A solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.8 g, 0.10 mole) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (13.3 g, 0.0333 mole) in 70 ml distilled water was added to a solution of Na_2CO_3 (31.8 g, 0.300 mole) in 300 ml distilled water at room temperature over about a 15-min period. The purple slurry was crystallized at 65°C overnight. Filtration, washing, and drying (125°C/vacuum) resulted in 13.2 g of an olive-green solid. The X-ray powder pattern was that of a diffuse hydrotalcite.

Anal. found: ash, 76.83%; Zn, 57.13%; Cr, 16.66%; C, 1.33%. Calculated for $\text{Zn}_6\text{Cr}_2(\text{OH})_{16}(\text{CO}_3^{2-}) \cdot 4\text{H}_2\text{O}$: ash, 73.12%; Zn, 59.60%; Cr, 15.80%; C, 1.33% (Zn and Cr on ashed basis).

Preparation of synthetic takovite (Ni^{2+} - Al^{3+}). An aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.1 g, 0.10 mole) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (12.5 g, 0.0333 mole) in 70 ml distilled water was slowly added to an aqueous solution of NaOH (24.0 g, 50% NaOH; 0.300 mole) and Na_2CO_3 (10.0 g) in 100 ml distilled water with good stirring at 30°C. At the end of the addition (20 min) a milky suspension remained.

Approximately half of this was heated in a stainless-steel bomb for 18 hr at 200°C, followed by filtration, water washings, and drying at 125°C/vacuum. This yielded a green solid which had an exceptionally sharp X-ray powder pattern.

Anal. found: ash, 67.76%; Ni, 60.28%; Al, 8.86%; C, 1.95%. Calculated for $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3^{2-}) \cdot 4\text{H}_2\text{O}$: ash, 70.11%; Ni, 64.09%; Al, 9.84%; C, 1.48% (Ni and Al on ashed basis).

The other half of this material was crystallized at 65°C/18 hr. After washing and drying (125°C/vacuum) this yielded a green solid which had a good hydrotalcite X-ray powder pattern.

Anal. found: ash, 62.77%; Ni, 59.38%; Al, 8.79%; C, 1.92% (Ni and Al on ashed basis).

Preparation of hydrotalcite with 1,12-dodecanedicarboxylic acid dianions. All operations were with deaerated water and under N_2 to keep out carbon dioxide.

A solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (85.8 g, 0.335 mole) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (56.34 g, 0.158 mole) in 210 ml distilled water was slowly added at 40°C to a solution of 1,12-dodecanedicarboxylic acid (19.5 g, 0.0756 mole), KOH (79.2 g "85%" pellets, 1.202 moles) in 600 ml of distilled water over a 1-hr period. This was carefully filtered and the cake added to a solution of the acid (39.0 g, 0.151 mole), KOH (20.1 g, 0.305 mole) in 600 ml distilled water and crystallized at 65°C/18 hr. The material was then filtered, washed neutral, and dried (125°C/vacuum). The X-ray powder pattern was diffuse.

Anal. found: ash, 47.59%; Mg, 31.67%; Al, 15.68%; C, 24.62%; N, <0.01%. Calculated for $\text{Mg}_6\text{Al}_{2.67}(\text{OH})_{17.3}[(\text{C}_2\text{H}_4)_2(\text{CO}_2^-)]_{1.34} \cdot 4\text{H}_2\text{O}$: ash, 44.24%; Mg, 36.33%; Al, 17.91%; C, 24.73% (Mg and Al on ashed basis).

The copper-aluminum double hydroxides could only be made using aqueous sodium bicarbonate solutions; at higher pH's the copper precipitated as copper hydroxycarbonates. In order to synthesize materials with noncarbonate anions, the sodium

carbonate was omitted and carbon dioxide-free conditions were employed. The presence of added anion (CrO_4^{2-} , SO_4^{2-} , NO_3^- , halide, PO_4^{3-} , etc.) during the synthesis and particularly during the crystallization is necessary.

Heat activation of these materials was done in air in a muffle furnace at $450 \pm 10^\circ\text{C}/18$ hr. Pulse reactor testing procedures were described elsewhere (14). Surface areas (BET/N_2), pore volumes (Hg penetration), transmission electron microscopy, X-ray powder patterns, Al-27-NMR-MAS, and X-ray photoelectron spectroscopy were carried out using standard instrumentation.

H-D exchange. The equipment used was

a $\frac{3}{8}$ -in. tubular reactor of 30-in. length, electrically heated and containing about 12–16 g of 50/80 mesh catalyst. A pump fed about 20 ml/hr ($\text{LHSV} = 1$) and the pressure was atmospheric. The catalyst charge was 16.0 g hydrotalcite, heat activated at 450°C , 18 hr in air, as 50/80 mesh particles.

Prior to feeding each organic (cyclohexane, toluene, *n*-propylbenzene, acetone), the column was heated at 450°C , 18 hr under nitrogen. Then, at 300°C , about 100 ml D_2O (99.8% D) was fed through the column (20 ml/hr, 5 hr). The catalyst was then dried $300^\circ\text{C}/\text{N}_2/18$ hr. Then, the organics were pumped through at the rate of ~ 20 ml/hr. The product condensate was collected separately every 10–15 min. This was analyzed

TABLE I
Pulse Reactor Results of Aldehyde and Ketone Aldol Reactions
over Thermally Activated Hydrotalcite Catalyst^a

Starting compound (2 μ l)	Product structures	area % (r.t., s)
		45 (104)
		2.1 (422)
		36.2 (955)
		7.5 (~1200)
		6.6 (1805)
		unknowns 9.4
		73.3 (287)
		16.5 (830)
		58.5 (578)
		12.9 (1303)
		23.9 (1449)
		unknowns 3.4
		19.7 (78)
		21.4 (212)
		34.1 (969)
		unknowns 20.0
		0.7 (68)
		89.4 (850)
		3.3 (1433)
		(3.8) unknowns
		47.2 (130)
		36.6 (605)
		unknowns 14.9

Note. First number is the area percentage of the structure; the number in parentheses is the retention time (sec).

^a 0.050 g, 50/80 mesh, 450°C heat-activated hydrotalcite. He ~ 30 cm³/min at 60 psi; 6-ft \times $\frac{1}{8}$ -in. 20% Carbowax 20M on 40/60 Chromosorb column; 70–210 $^\circ\text{C}$ at 8 $^\circ\text{C}/\text{min}$ then c.t.; FID detection. Acetonitrile was unreactive; esters deactivate the catalyst stoichiometrically. Further experimental details are in Ref. (14).

TABLE 2

Heterometal-Substituted, Thermally Activated Hydrotalcites and Their Catalytic Activities

M^{2+}	M^{3+}	M^{2+}/M^{3+}	Crystallization		Pulse reactor results ^a		Comments
			Temp. (°C)	X-Ray data ^b	Acetone conv. (%)	MSO/I ^c	
Mg	Al	3	65	fg HT	40	0.06	—
Ni	Cr	3	65	vw HT	20	20	— ^d
Ni + Mg	Al	3	65	vg HT	37	0.29	—
Mg	Al + Cr	3	65	w HT	30	1.3	—
Ni	Al	3	65	fg HT	25	7.1	— ^d
Ni	Al	3	65	g HT	34.7	1.3	— ^d
Ni	Al	3	65	vg HT	18	3.5	— ^d
Zn	Cr	3	65	w HT	10.4	7.5	—
Co	Cr	3	65	— ^e	14	— ^f	All MSO
Zn	Cr	3	65	w HT ^g	11.1	55	—
Co	Al	3	65	fg HT	21	7.1	—

^a 450°C/air/18 hr heat-activated catalyst. Experimental technique is in Ref. (14).

^b HT = hydrotalcite; vw = very weak; fg = fairly good; vg = very good; w = weak.

^c MSO = mesityl oxide; I = isophorone.

^d Mostly 1,3,5-trimethylbenzene.

^e Strong fluorescence.

^f No isophorone produced.

^g Only Na₂CO₃ as base, no sodium hydroxide used during synthesis.

by gas chromatography–mass spectroscopy.

Olefin isomerization–aromatization. The same reactor was used containing, instead, 12.92 g of 50/80 mesh catalyst. The filled reactor was again heated 450°C/N₂/18 hr, then cooled to 300°C and the olefin was pumped in at 20 ml/hr. Analysis were by gas chromatography using a 10-ft × $\frac{1}{8}$ -in. 20% Carbowax-20M column with appropriate temperature programming.

Nucleophilic aromatic substitution. A hydrotalcite was prepared from magnesium and aluminum nitrates and sodium hydroxide in the presence of potassium fluoride; crystallization was at 65°C, etc. This yielded a material which analyzed as Mg₆Al_{2.20}(OH)_{16.4}(CO₃²⁻)_{0.6}(F)_{1.0} · 4H₂O and had a good hydrotalcite X-ray powder pattern. This was heat activated at 400°C, 18 hr, in air.

Five grams of this powder was heated in dimethyl sulfoxide (25 ml) and xylenes (25 ml) containing 0.5 g of 2,4-dinitrochloro-

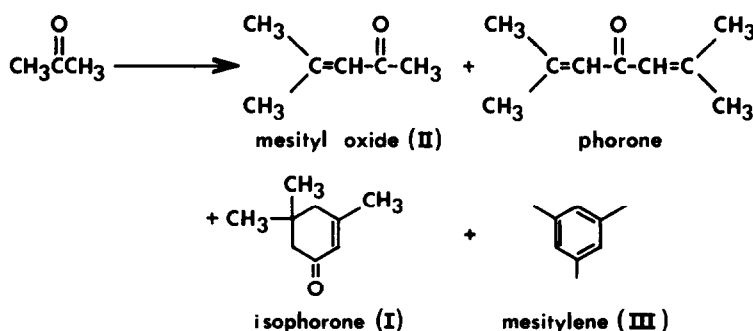
benzene for 18 hr under nitrogen at 154°C. The gas chromatographic analyses showed no fluoro-substituted compound. A good deal of decomposition appeared evident, so the reaction was repeated with the omission of the DMSO but with the same results.

RESULTS AND DISCUSSION

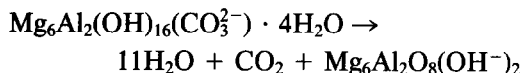
Table 1 illustrates the reactions of ketones and aldehydes in the pulse reactor (14) as catalyzed by the heat-activated hydrotalcite (Mg/Al ≈ 2.2). Each compound yields the expected aldol dimer or trimer based on known chemistry (13). It is quite likely that with a more appropriate choice of temperature and contact time, the efficiencies to the desired product(s) could be greatly enhanced.

Table 2 illustrates the effects due to variation of the M^{2+} and/or M^{3+} metals when acetone is used as reagent. In all cases, other than that for $M^{2+} = \text{Mg}^{2+}$ and $M^{3+} = \text{Al}^{3+}$, there is a substantial decrease in the

isophorone (I) production and, instead, a large amount of its precursor mesityl oxide (II) is made. Also, in most cases there is a substantial drop in the catalyst's activity. Since acetone oligomerization is a sequential reaction, it would stand to reason that a drop in the acetone conversion would increase the yield of (II) relative to that of (I). Catalysts containing nickel all yield fairly large quantities of mesitylene (III) along with some (I) and (II). This is due to the



The interstitial anion in these hydrotalcites dramatically affects the conversion of acetone. The normal catalyst ($\text{Mg}/\text{Al} = 3$; CO_3^{2-} hydrotalcite) yields a highly active catalyst on heat activation at 450°C ($\sim 40\%$ acetone conversion, Table 1). When, instead, the hydrotalcite contains sulfate, halide, or chromate, then, on heat treatment, materials are obtained which are substantially inactive. The heating of carbonate-hydrotalcite should yield only a hydroxyl-containing product with the loss of water and the anion (as carbon dioxide).



In the case of sulfate, halide and chromate, etc., this elimination of the anion cannot take place (at 450°C); it is irreversibly bound to the skeleton of the residue in place of the catalytically effective hydroxyl group. Hence, hydrotalcites, etc., with "nonvaporizable" anions will lead to catalytically inactive substances.

This would then require that only vapor-

dehydrogenating and dealkylating properties of nickel-containing catalysts. Materials containing chromium tend to have high ratios of mesityl oxide to isophorone. Cobalt-containing catalysts produce much mesityl oxide and little isophorone and, unexpectedly, virtually no mesitylene. Clearly, variation of the M^{2+} and M^{3+} results in large changes in the product spectrum.

izable anions ($450^\circ\text{C}/\text{air}$) should result in active catalysts. This is indeed the case: nitrate, acetate, oxalate are expelled as oxides of nitrogen or water and carbon dioxide on heating and yield very active catalysts with acetone (NO_3^- , 28%; oxalate, 32%; valerate, 44% conversion in the pulse reactor; carbonate, 40%). It is important to recognize that for the removal of some anions, the alkyl carboxylates, for example, the presence of oxygen and heat are needed, while with the carbonate and nitrate only heat is required to make an active catalyst.

It has been demonstrated elsewhere (18) that the size of the interstitial anion affects the interstitial d -spacing (006 plane). Thus, the incorporation of α,ω -dicarboxylic acid dianions as interstitial anions in a hydrotalcite-type lattice ($\text{Zn}^{2+}-\text{Al}^{3+}$) gave rise to a d -spacing (006 plane) of 9.2 \AA for the oxalate dianion (C_2) and close to 19 \AA for the sebacic acid dianion (C_{10}). The incorporation of similar anions in the $\text{Mg}^{2+}-\text{Al}^{3+}$ hydrotalcite should pry apart the individual $\text{Mg}-\text{Al}-\text{OH}$ layers and possibly give rise to

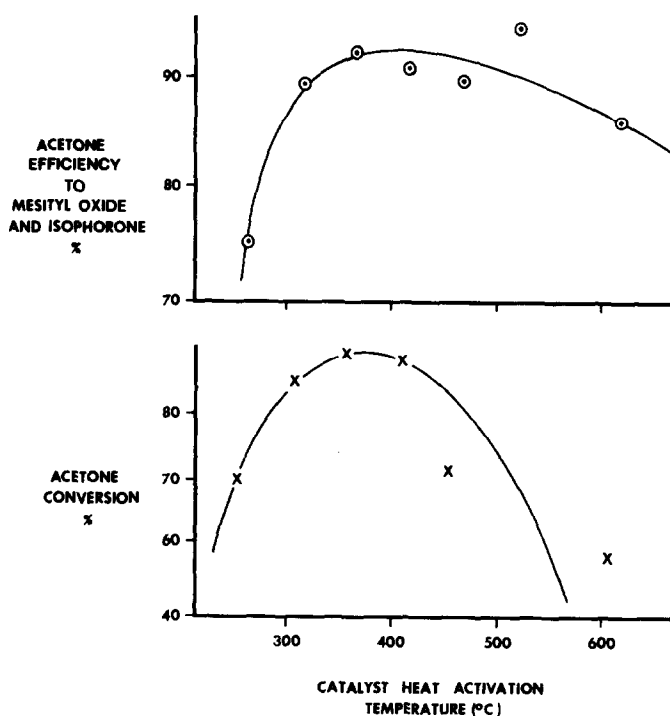


FIG. 1. Effect of heat treatment on hydrotalcite catalyst activity and specificity ($Mg/Al \approx 3$) pulse reactor results, conditions as per Table 1.

truly large surface areas, and hence, high catalytic activities on thermal-oxidative activation. Table 3 shows the results which were obtained when oxalic, adipic (C_6), 1,10-decane (C_{12}), and 1,12-dodecanedicarboxylic (C_{14}) acid dianions were incorporated into the lattice as interstitial anions (some nitrate always appeared to be present as judged by the nitrogen analyses). Relative to the carbonate hydrotalcite (36% conversion), these thermally activated materials were more active, but not dramatically so (C_2 —45, C_{12} —45, and C_{14} —56% pulse reactor acetone conversion), while the adipic acid (C_6) dianion resulted in a somewhat less active catalyst (29% conversion). Oddly, the continuous (30 cm^3) reactor results show that the C_{12} diacid dianion-derived product was almost three times as active (32.4%) as the carbonate hydrotalcite (12.9% acetone conversion). These results are probably due to the fact that the surface areas of these catalysts do not differ

substantially (carbonate—210; C_{12} diacid—239, and adipic acid—233 m^2/g , BET/ N_2) and, therefore, do not result in greatly enhanced activities. Transmission electron micrographs of the C_{14} dianion-derived hydrotalcite and its heat-activated product show very thin platelets (0.02 μm) which have not expanded during the heating process.

The temperature at which the hydrotalcite is activated affects the catalytic activity strongly. The unheated $Mg^{2+}-Al^{3+}-CO_3^{2-}$ hydrotalcite is not catalytically active. Figure 1 illustrates the pulse reactor results of a variably heated hydrotalcite. Clearly, there is a maximum in the temperature region 400–450°C for both the activity (% acetone conversion) as well as the selectivity (efficiency to (I) and (II)). Similarly, it could be expected that the Mg/Al ratio would have an effect on the catalyst. Table 4 shows that this does not appear to be so, at least not to a substantial degree.

TABLE 3
Effect of Large Interstitial Anion on Catalyst Activity^a

Anion	Crystal- lization temp. (°C)	Analytical results ^b			X-Ray ^c	Pulse testing results ^f		Surface area (BET/N ₂ ; m ² /g)	Continuous reactor (30 cm ³) results						
		Mg ₂ Al ₂ (OH) _{12+2n} (A ⁻²) _x (NO ₃) _y · 4H ₂ O	n	12 + 2n		x	y		Conv. ^d (%)	MSO/l (wt)	Tetralone (%)	Temp. (°C)	Conv. (%) ^e	Eff. MSO/l (wt)	
Adipic ²⁻ 1,10-Decane- dicarboxylic ²⁻	65	2.69	17.4	0.95	0.80	Poor	HT	29.1	0.16	1.2	233				
1,12-Dodecane- dicarboxylic ²⁻	65	3.00	18.0	2.8	0.2	Fair	HT	44.7	0.028	2.3	—	308	32.4	74.3	0.055
Oxalic ²⁻	65	2.67	17.3	1.3	<0.01	Poor	HT	55.5	0.010	2.2	239				
Oxalic ²⁻	60	3.14	18.3	1.5	—	—	—								
Oxalic ²⁻	67	4.34	20.7	2	—	HT + ?		45.1	0.056	2.1	—	330	14	88	0.357
CO ₃ ²⁻	65	2.02	—	—	—	Good	HT	36.2	0.125	2.0	210	320	12.9	91	0.208

^a Heat-activate 450°C/air/18 hr.

^b Calculated from % ash, Mg, Al, C. A⁻² is the respective dianion.

^c X-Ray powder diffraction data: HT = hydrotaelite; ? = diffraction lines of unknown origin.

^d Total acetone conversion to other products.

^e Efficiency to mesityl oxide (MSO) and isophorone (I).

^f Pulse reactor conditions as per Table 1.

TABLE 4

Effect of Variation of Hydrotalcite Mg/Al Ratio on Catalytic Activity^a

Catalyst	1.39	1.33	2.24	2.27	3.04	6.27
Mg ²⁺ /Al ³⁺	1.39	1.33	2.24	2.27	3.04	6.27
X Ray ^b	HT ^c	HT	HT	HT	HT ^d	HT ^e
Carbon found (%)	2.22	NA	2.50	2.25	2.36	1.42
Catalytic activity						
Acetone conv. (%)	37.5	21.0	24.6	15.0	22.5	24.2
Conv. eff. (%)	83.8	85.6	76.3	88.9	81.0	91.1

^a Preparations were carried out as per experimental except Mg-Al ratios were varied. Pulse reactor results, conditions as per Table 1.

^b HT = hydrotalcite.

^c Plus Al(OH)₃.

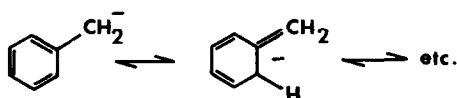
^d Includes a trace of hydromagnesite Mg₂(OH)₂CO₃.

^e Plus some Mg(OH)₂.

H-D Exchange

Hydrogen-deuterium exchange studies frequently yield valuable information regarding certain catalytic properties. In this particular case, carbon-bound H-D exchange indicates approximately the base strength of the strongest hydroxyl group. Four molecules were examined for their ability to exchange carbon-bound hydrogen for surface-bound deuterium (presumably as -OD). Both acetone and toluene exchanged all hydrogens² for deuterium (Table 5). This indicates that the catalyst is a base (19) strong enough to remove a proton from the toluene methyl group ($pK_a \approx 35$). The lack of exchange with cyclohexane is due to the inability of the catalyst to extract a proton from this molecule ($pK_a \sim 45$). Hence, the catalyst's base strength is between 35 and 45. The nonexchange with *n*-propylbenzene may be due to steric factors—the benzylic hydrogens are too hindered to get to the catalyst's surface in order to exchange.

² The exchange of toluene ring hydrogens is due to C₆H₅CH₂⁻ anion interaction with the ring,



Thereby, the ring hydrogens are also exchanged (20).

TABLE 5

H-D Exchange over Deuterated Catalysts^a

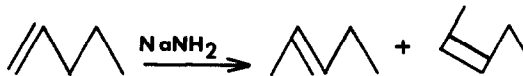
Compound	Structure	pK _a (19)	Exchange (300°C)
Cyclohexane		45	-
Toluene		35	+
<i>n</i> -Propylbenzene		35	-
Acetone		20	+

^a 30-cm³ reactor; catalyst was the Mg-Al-CO₃²⁻ HT, activated at 450°C followed by treatment with 99% D₂O for 5 hr at 300°C.

The toluene H-D experiments were conducted (at 300°C) with dry toluene and the deuterated catalyst. Analyses (mass spectroscopy) showed that 0.1102 equivalents of deuterium had exchanged, which represented 232% of theory.³ Presumably, the catalyst still contains an appreciable amount of strongly adsorbed D₂O which cannot be removed even at 300°C and dry nitrogen flow for 18 hr (atmospheric pressure).

Olefin Isomerization—Aromatization

Very strong bases are known to isomerize olefins having allylic protons (21).

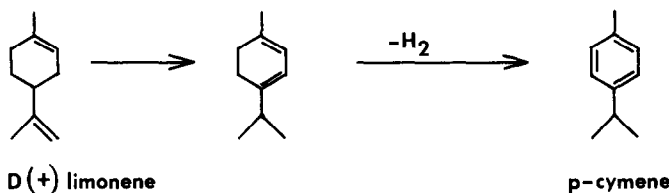


These strong bases also do not cause skeletal isomerization as the acid catalysts do.

³ The 12.95 g of catalyst [Mg₆Al_{1.89}(O)_{7.89}(OH/D)_{1.33}(CO₃²⁻)_{0.28}] had 0.0475 eq H/D based on the above formula; 0.1102 eq of H/D was found to have exchanged by material balance of the product acetone-d⁶.

The reaction mechanism, in the case of base-catalyzed isomerization, is thought to be allylic proton abstraction, followed by

double-bond isomerization and readdition of the proton. Cyclic diolefins not only isomerize but also aromatize:



The thermally treated (450°C/N₂/18 hr) hydrotalcite catalyst has been tested as a possible catalyst for reactions of this type. When a freshly activated catalyst was contacted with these olefins, little isomerization or aromatization took place (Table 6). 1-Pentene isomerized to about 8.9% *cis*- and *trans*-2-pentene. The thermodynamic equilibrium is 1-pentene 1.6 wt%, *cis*-2-

pentene 26.4%, and *trans*-2-pentene 72.0% (22). The limonene suffered very little change; 92.1% was recovered unchanged and the only recognizable product was *p*-cymene (1.7%) with 2.0 and 4.3% of other products present. The very labile 1,4-cyclohexadiene isomerized to the 1,2 conjugated material (14%), along with a trace of benzene.



Clearly, at 300°C, this material is not a good olefin isomerization catalyst; this catalyst is not sufficiently basic to abstract the allylic protons in order to initiate the reac-

tion (CH₂=CH—CH₃, pK_a ~ 36) (23). It is interesting to observe that the only compound which did isomerize to an appreciable extent was the 1,4-cyclohexadiene.

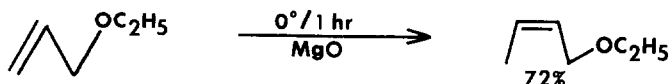
TABLE 6

Olefin Isomerization and Aromatization Experiments ^a				
Olefin used	Results compd. (Area %)			
<chem>CC=CC</chem>	<chem>CC=CC</chem> (91.1)	<chem>CC=CC</chem> (3.6)	<chem>C=CC</chem> (5.3)	
<chem>CC(C)=C1C=CC=CC1</chem>	<chem>CC(C)=C1C=CC=CC1</chem> (92.1)	<chem>CC(C)=C1C=CC=CC1</chem> (1.7)	<chem>CC(C)C1=CC=CC=C1</chem> (2.0)	<chem>CC(C)C1=CC=CC=C1</chem> (4.3)
<chem>C1=CCC=CC1</chem>	<chem>C1=CCC=CC1</chem> (81.7)	<chem>C1=CC=CC1</chem> (13.9)	<chem>C1=CC=CC=C1</chem> (0.5)	

^a 30-cm³ reactor, 300°C; LHSV ~0.7–1.2.

Here, the 3- and 6-positioned allylic protons must be much more acidic than those of propylene; hence, the reaction takes place, albeit slowly. Similar catalysts

(MgO, CaO, SrO) are able to isomerize allyl ethers at surprisingly low temperatures (24):



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