Clay-activated isomerization reactions

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I. INTRODUCTION

Natural clays were among the earliest solid acid catalysts used in the oil industry to promote cracking and isomerization reactions. Not long after their introduction in the late 1930s, they were replaced in large part by synthetic amorphous silica–aluminas, which gave more consistent results. During the 1960s the amorphous catalysts were superseded by the more active and shape-selective microporous crystalline aluminosilicates known as zeolites. However, there has been a renewed interest in the use of clays as catalysts because zeolites are not as suitable for the conversion of relatively large molecules. This interest resulted in the synthesis of highly active clays and in the development of the pillared clays, in which the useful surface has been increased and shape selectivity created by separating the layers with the aid of large cationic clusters (pillars).

It is well known that most of the observed catalytic properties of clays are due to their acidic character. Therefore, this chapter starts with a short summary of methods to determine these acidic properties and the main results of these methods. Then the various steps to obtain an active catalyst are discussed, such as synthesis, purification, and activation. This is followed by a discussion of the mechanism of the isomerization reaction and a review of the use of clays as isomerization catalysts.
II. ACIDIC PROPERTIES OF CLAYS

For details of structures of clay minerals and their characterization by x-ray diffraction, we refer to Chapter 11 in this volume. The other characterization methods are fully covered in the monographs of Weaver and Pollard (1973), Theng (1974, 1982), and van Olphen (1977).

The acidity of solid surfaces can be determined by using the well-known Hammett indicators (Tanabe, 1970). This simple technique gives only qualitative information about the number and distribution of acidic sites. More quantitative data can be obtained by monitoring at various temperatures the adsorption of a base such as ammonia, trimethylamine, and pyridine. In combination with IR spectroscopy it is even possible to distinguish between Brønsted and Lewis acidity. For example, the IR spectrum of pyridine adsorbed on Lewis sites differs considerably from that of the pyridinium ion that is formed on Brønsted sites (Aldridge et al., 1965; Barrer, 1978). The work of Plee et al. (1985) corroborate nicely the previously mentioned features. They observed that the acidity of calcined beidellite compared well with Y zeolite, while the calcined montmorillonite-based catalyst was much less acidic. With IR spectroscopy it was shown that on beidellite mainly Brønsted sites occurred, while montmorillonite exhibited a much lower acidity which was mainly of the Lewis type.

In conclusion, it emerges that the acidic properties are strongly dependent on the type of clay, the exchanged cation, and the H$_2$O content.

III. METHODS OF CATALYST PREPARATION

A. Purification of Natural Clays

Natural clays often contain quite large amounts of impurities, which should be removed to prevent interference with the catalytic function. As the variation in amount and type of impurities is as large as the variation in clay types, it is not possible to give here a specific purification recipe. Therefore, we limit ourselves to some general remarks and refer to the literature for experimental details (van Olphen, 1977).

Each purification method should involve separation of coarse mineral impurities from the clay. This is best achieved by suspending the sample in water and allowing the large particles to settle. The clay particles can then be siphoned off (van Olphen, 1977). If the sample contains a relatively large amount of organic material, the dry material can be brought in contact with concentrated hydrogen peroxide. Several methods exist for the removal of inorganic impurities. For instance, carbonates and free ferric oxide can be removed by a subsequent treatment with sodium acetate buffer solution and sodium dithionite/sodium citrate (Tzou, 1983).

B. Activation Procedure

The first step in the activation procedure, which is required for both natural and synthetic clays, is to convert the clay into the desired ion form. In the case of metal ions, this can be done with relative ease by ion exchange using a concentrated solution of a suitable salt. The excess salt can be removed by repeated washings employing a centrifuge, followed by dialysis. As an alternative, one can use ion-exchange resins in the suitable ion form. In contrast, it is not as easy to prepare the H$^+$ form of a clay via ion exchange with an acid or a resin in the H$^+$ form. The acid attacks the clay structure and part of the aluminum in the structure is transferred to
ion-exchange sites. This effect occurs even under relatively mild conditions. For example, van Olphen (1977) found that the conversion of Wyoming bentonite (montmorillonite) with 0.01 N HCl at room temperature led to the occupation of 60% of the exchange sites by Al. The best way to overcome this acid leaching problem is to prepare the NH₄⁺ form via ion exchange, followed by a heat treatment at 550°C (Wright et al., 1972). The NH₄⁺ ion will decompose, leaving an H⁺ ion on the clay. By performing the heat treatment in air all of the residual organic material will be burnt off, which results in a ready-to-use acidic catalyst.

C. Synthetic Clays

The main incentive for using synthetic clays is that several interesting materials are either not available in sufficient quantities in their natural form (beidellite) or do not exist in nature. Most clays can be synthesized via hydrothermal methods (Barrer, 1982). Here we discuss briefly the synthesis of clays that have been used for isomerization reactions.

Koizumi and Roy (1959) have prepared in a pressure vessel at 300°C and 1000 bar, starting with a stoichiometric gel, 100% beidellite with the composition Na₆.₃₃Al₂(Si₃.₆₇Al₀.₃₃O₁₀)(OH)₂. The very high pressure poses a problem for large-scale preparation of the clay. However, Diddams et al. (1984) claim that the reaction also proceeds at 300°C and autogenous pressure.

Granquist (1966) described the synthesis at ~300°C of a novel high-surface-area (140–160 m²/g) clay with randomly interstratified mica- and beidellite-type layers having the following approximate formula: Na₆.₆₉Al₂(Si₃.₆₇Al₀.₃₃O₁₀)(OH)₂. This clay has become known as synthetic mica montmorillonite (SMM), although it does not contain any montmorillonite but only beidellite. It was found that partial incorporation of nickel into the octahedral positions of the SMM structure resulted in a dramatic increase in acidity. This became apparent only after reduction of the nickel to the zero-valent state (Swift, 1977; Heinerman et al., 1983; Robschlager et al., 1984). In the original NiSMM synthesis (Granquist, 1974) a relatively large excess of H₂O had been used, which resulted in an inefficient use of the high-pressure autoclave. Heinerman (1985) reported an improved synthesis, which involved the use of (commercial) amorphous silica–alumina as starting material and minimum quantities of water. This resulted in a yield that was three times higher per reaction mixture volume.

Synthesis of trioctahedral clays, where all octahedral positions are occupied with cations, is, in general, somewhat less difficult than the preparation of the dioctahedral materials, where two out of three octa-

hedral positions are filled with cations. For example, chrysotile (trioctahedral) can be prepared by heating a mixture of the appropriate oxides and an excess of H₂O at 250°C for 24 h (Robson, 1973, 1974), whereas preparation of dioctahedral isomorphous kaolinite requires more severe conditions (Barrer, 1982). Furthermore, Sohn and Osaki (1980) have claimed that nickel–talc [−Ni₃Si₄O₁₀(OH)₂] can be synthesized by precipitation from an acidic solution of a nickel salt–sodium silicate mixture at temperatures as low as 60°C.

Several interesting materials, known as fluorine micas, have been synthesized by employing salt melts as crystallization medium or via a solid-state reaction (Shell and Ivey, 1969; Kitajima et al., 1984). One example is a material with the structural formula NaMg₂.₃0.₅(Si₆O₁₀)F₂, which is swellable in water (Kitajima and Daimon, 1975). Here the charge imbalance is not due to isomorphous substitution but to vacancies in the octahedral layer. Morikawa et al. (1983a) have shown that this material in the Na form is inert, in contrast with other alkali-neutralized clay materials which exhibit some residual acidity. It is, therefore, ideal to study the intrinsic activity of metals and metal ions.

D. Pillared Clays

Pillared clays are materials that are modified by exchanging the interlamellar cations for bulky ions designed to provide increased access to the interior region and shape selectivity at temperatures where water or other solvents are thermally removed. Work on pillaring started by ion exchanging with organic cations such as ethylene–diammonium. This was only partially successful because the ion intercalated with its long axis parallel to the clay layers which resulted in a layer separation of only 0.28 nm (Barrer and MacLeod, 1955). A clear advance was the use of the cage-like molecule 1,4-diazobicyclo[2.2.2]octane (DABCO), which resulted in an interlayer distance of 0.53 nm (Mortland and Berkheiser, 1976; Shabtai et al., 1977). However, the thermal stability of these materials appeared to be unsatisfactory. Therefore, attention shifted to inorganic materials as pillars. The best results were obtained with polymeric cationic complexes of aluminum. Several preparation methods have been reported, all of which resulted in samples with a surface area of 200–400 m²/g and a layer separation of 0.9 nm. All procedures start with the preparation of well-dispersed clay slurries using purified <2-μm materials. The main difference between the methods is the concentration of the clay suspension. For instance, Lahav and Shani (1978) and Lahav et al. (1978) added dropwise aged aluminum hydroxide solutions, prepared with AlCl₃ and NaOH (OH/Al = 1.85), to
stirred montmorillonite suspensions of only 50–200 mg/L. After flocculation occurred, the resulting material was allowed to settle for several hours and was collected by centrifugation. The main disadvantage of this procedure is the necessity to handle large volumes of suspension. Vaughan et al. (1979, 1981; Vaughan and Lussier, 1980) brought much higher clay concentrations (>27 g montmorillonite or beidellite/L) in contact with solutions containing aluminum hydroxy oligomers at temperatures of the order of 60°C for about 30 min. The most convenient oligomer source is a commercial aluminum chlorhydride known as Chlorhydrol (supplied by Reheis Chemical Company). After pillaring the material should be washed thoroughly in order to obtain an active material. Comparable methods have been reported by Gaa and van Santen (1984) and Gaa et al. (1983) for NiSMM pillaring, and Ple et al. (1985) for beidellite pillaring. Similar clay concentrations have been used by Jacobs et al. (1984), who achieved pillaring by dialyzing clay–aluminum hydroxy slurries at room temperature for 4 days. After the actual pillaring it is necessary to give the material a heat treatment at about 550°C, which probably covalently binds the pillaring agents to the clay layer. The material can now be brought in the desired (active) ion form. Alternatively, one can try to pillar the active ion form of the clay. However, this is not always possible because the swelling depends on the type of interlamellar ion (Barrer, 1978).

Novel pillars with interesting properties have been described in the literature. Chromium oxide pillars, where chromium oxide has intrinsic hydrogenation activity, have been claimed to give larger pore size (Tzou, 1984; Pinnavaia et al., 1985). Other novel pillaring materials are silicon oxide (Lewis et al., 1985), zirconium oxide (Yamanaka and Brindley, 1979; Vaughan et al., 1979, 1981; Kikuchi et al., 1985), titanium oxide (Vaughan et al., 1979), and nickel oxide (Tamanaka and Brindley, 1978). Silicon pillars appear to have better hydrothermal stability and have been used in the preparation of an isomerization catalyst.

IV. ISOMERIZATION REACTIONS

A. Reaction Mechanism

The isomerization of hydrocarbons over solid acidic catalysts has been studied extensively. It is now generally accepted that the reaction mechanisms involve carbonium ions. The factors that determine the selectivity of the reaction are well known as well. Therefore, we give here only a short review of the relevant principles.

The first step is formation of a surface carbonium ion. This intermediate can undergo rearrangements by hydrogen-atom and/or carbon shifts. The former operates in the case of double-bond isomerization. The latter results in skeletal isomerizations of the type given below (Brouwer and Hogeveen, 1972):

\[
\text{C} = \text{C} \rightarrow \text{C} = \text{C} \rightarrow \text{C} - \text{C} \rightarrow \text{C} + \text{C}
\]

The driving force is the relatively high stability of the tertiary carbonium ion compared with the other ions.

Carbonium ions can be formed via several routes:

1. Protonation of unsaturated bonds by Brønsted acidic sites (Weisz, 1970; Kouwenhoven, 1973);
2. Abstraction of a hydride (H⁻) ion by a Lewis acidic site (Nace, 1969); and
3. Protonation of saturated compounds at Brønsted sites has been claimed to give five-coordinated carbon atoms (nonclassical carbonium ion) followed by the formation of molecular hydrogen and a classical carbonium ion (Olah, 1973).

The first route, protonation of unsaturated hydrocarbons, proceeds with relative ease compared with the other mechanisms. For that reason lower temperatures can be used, which gives less (thermal) cracking and therefore higher selectivities.

To achieve similarly high selectivities with saturated compounds, the concept of bifunctional catalysis has been developed, in which a (de)hydrogenation function (for instance, a noble metal) is combined with an acidic support (Sinfelt et al., 1960). The dehydrogenation function produces alkenes resulting in a lowering of the reaction temperature. According to Coonradt and Garwood (1964), the highest selectivities are obtained when there is a balance between the (de)hydrogenation activity and the acidity of the catalyst. Fast dehydrogenation (relative to the isomerization reaction) results in a relatively high steady-state concentration of unsaturated compounds. These compounds displace the isomerized carbonium ions from the acid sites by competitive adsorption, thus limiting the residence time on the catalyst, which reduces the chances of β-scission of branched carbonium ions. Furthermore, fast hydrogenation of the desorbed rearranged alkenes prevents readsorption and hence removes the possibility of β-scission. The validity of this balance concept has been verified.
experimentally demonstrated for several types of acidic supports. For instance: Pt/SiO₂-Al₃O₃ (Coonradt and Garwood, 1964), Pt ultrastable Y zeolite (Jacobs et al., 1980), and NiSMM (Robschlager et al., 1984).

In the preceding mechanism, isomerization and β-scission (cracking) are consecutive reactions. It is well known in the field of reactor engineering that the highest yield of the intermediate (in this case isomerized) product is obtained in a reactor configuration where mixing of product is kept to a minimum, i.e., plug-flow operation (Levenspiel, 1972), while mixing in a batch-type operation leads to an increased contribution of consecutive reactions.

### B. Alkene Isomerizations

In this section we only deal with gas-phase double bond isomerization of butenes. Other alkene reactions will be discussed by J. Adams in Chapter 27. This rearrangement of butenes is a typical test reaction to detect even the weakest (Brønsted) acidic sites.

The importance of the presence of H₂O in the formation of Brønsted sites in layered silicates without tetrahedral substitution (no intrinsic Brønsted acidity) has been shown by Sohn and Ozaki (1980) for a nickel–talc-like structure [Ni₃Si₄O₁₆(OH)₂]. They found that the activity for 1-butene isomerization (at a temperature as low as 20°C) peaks at a pretreatment evacuation temperature of 100°C. The activity ran closely parallel with the Brønsted surface acidity as measured by n-butylamine titration in benzene. At an evacuation temperature of 400°C the catalyst was quite inactive and hardly any Brønsted sites could be detected.

That there are still Brønsted sites present in a tetrahedrally substituted SMM clay (NL Industries, Baroid division) even after activation at 530°C in vacuum has been demonstrated by Hattori et al. (1973). They performed tracer studies with deuterated SMM and nondeuterated butene in a pulse reactor at ambient temperatures under water-free conditions. They inferred from the appearance of deuterium in the reaction products that Brønsted sites in layered silicates without tetrahedral substitution (no intrinsic Brønsted acidity) have been shown by Sohn and Ozaki (1980) for a nickel–talc-like structure [Ni₃Si₄O₁₆(OH)₂]. They found that the activity for 1-butene isomerization (at a temperature as low as 20°C) peaks at a pretreatment evacuation temperature of 100°C. The activity ran closely parallel with the Brønsted surface acidity as measured by n-butylamine titration in benzene. At an evacuation temperature of 400°C the catalyst was quite inactive and hardly any Brønsted sites could be detected.

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The isomerization of cis-2-butene at 150°C over 1,4-diazobicyclo-[2,2,2]octane (DABCO)-exchanged Zn-montmorillonite has been used by Stul et al. (1983) to show that pillaring could make more sites accessible to catalysis. They observed a fourfold increase in initial activity due to the pillaring.

Morikawa et al. (1983b) used a conventional pulse reactor to convert 1-butene to cis- and trans-2-butene (at 380°C/He flow) over fluorotetrasilic micus (TSM, Topy Industries) exchanged with several metal ions such as Mg²⁺, Al³⁺, Pt²⁺, etc. The Pt²⁺-exchanged sample was the most active with 70% conversion and 85% selectivity. From the relatively low ratio of trans-2- to 1-butene (~1) in the products after cis-2-butene isomerization it was concluded that no Brønsted acid site was involved in the reactions. Furthermore, no relation could be found between known Lewis strengths of the ions and the activity. The use of hydrogen instead of helium as a carrier gas resulted in a marked increase in activity, which strongly indicates that the reaction proceeds on the metal ions via the type of half-hydrogenated species well known in the field of metal and metal complex catalyses (Anderson, 1973).

### C. Paraffin Isomerizations

The skeletal isomerization of n-paraffins is an important reaction especially for the oil industry. For instance, isomerization of paraffins in the light gasoline boiling range results in an increase in octane number. Most work on this reaction has been done with zeolites and γ-Al₂O₃ doped with F and/or Cl (to induce acidity). Clay like materials, i.e., synthetic and pillared clays, have been evaluated as substitution for zeolites to overcome the pore diffusion and steric occlusion problems encountered with microporous materials.

In Table I we have summarized the catalysts that have been used for paraffin conversion, together with the relevant data regarding conversion and conditions. The following points deserve further comment:

1. A relatively high hydrogen pressure has been applied (except in two cases). The rationale is prevention of deactivation due to coke formation on the catalyst surface.
2. The most active clay catalyst, i.e., NiSMM doped with Pd or Pt, can have an activity comparable to that of the very active 1% Pd–H mordenite (compare nos. 7, 8, and 11).
3. The high activities are combined with very high selectivities which indicates a bifunctional mechanism.
4. The very poor performance of natural montmorillonite can be improved markedly by pillaring with an Al oligomer prepared in this case via dialysis (compare nos. 14 and 15). Whether the activity of the pillared clay is comparable with Pt–NiSMM (no. 13) is questionable because Jacobs et al. (1984) used a very low H₂ pressure. This normally results in a relatively high initial activity (high alkene concentration) followed by a rapid (coke) deactivation.

The best area for clays as catalysts is the conversion of large molecules as demonstrated by the work of Shabtai et al. (1981) on cracking of perhydrophenanthrene over a Ce-exchanged, Al-pillared montmorillonite.
They observed a markedly higher activity of the pillared clay as compared to Y zeolites, while the opposite was found for smaller molecules.

D. α-Pinene Isomerization to Camphene

The effectiveness of various clays for the production of camphene, a raw material for camphor production, has been studied since the 1930s. Tischchenko and Rudakov (1933) used an unspecified clay activated with 10% hydrochloric acid for the α-pinene (I) rearrangement to camphene (II) and obtained a 62% yield:

\[
\text{Wagner—Meerwein rearrangement}
\]

\[
\text{II}
\]

Nazir et al. (1976) reported a more detailed investigation with china (kaolin-type) and fire clay samples from Pakistan. The best yield (60%) was obtained with a china clay treated with hot concentrated sulfuric acid. The reaction was carried out at 110°C with 2% by weight catalyst in a stirred round-bottom flask. Other clays catalyzing camphene production are H- and Al-montmorillonite (Dupont and Dolou, 1948; Ovcharenko, 1982), H-vermiculite, H-kaolinite, and H-hydrous mica (Battalova et al., 1977). In all cases yields of around 60% were obtained.

E. Cholesterol Rearrangement

During studies concerning the origin of polycyclic compounds present in sediments, shales and crude oils by the group of Albrecht at Strasbourg (Sieskind and Albrecht, 1985) it was discovered that cholest-5-ene (III) could be converted quantitatively to backbone-rearranged 20-R and 20-S-cholest-13(17)-enes (IV) at room temperature in the presence of dry K-10 montmorillonite (FLUKA):
Unfortunately, the “dryness” was not specified. A typical experiment was done in the following way: 750 mg of reactant was added to the same amount of clay suspended in 6 mL of dry cyclohexane, and the mixture was stirred for 1 h. Without the clay catalyst this reaction proceeds only under superacidic conditions, e.g., p-toluene sulfonic acid at reflux temperature. Furthermore, the reported yields are only of the order of 50% (Blunt et al., 1969; Kirk and Shaw, 1970). So we have here a clear example of a very effective clay catalyst.

F. Oleic Acid Isomerization

Montmorillonites are industrially used as catalysts for the dimerization of unsaturated fatty acids to dicarboxylic acids (Johnston, 1944). Sometimes considerable amounts of isomerized products can be found in the reaction products. Nakano et al. (1985) observed that heating oleic acid at 230°C for 3 h with a montmorillonite clay (Alabama Blue Clay) gave a branched chain isomer yield of 27%. Adding water increased the yield by 10% (higher Brønsted acidity). On (CH₃)₄N pillared montmorillonite mainly cis–trans isomerizations took place, which was probably due to induced shape selectivity (Weiss, 1981).

V. CONCLUSIONS

We did an extensive literature search on clay-catalyzed isomerization reactions. It appears that clays have only scarcely been used in synthetic organic chemistry reactions, while much more effort has been devoted to the industrially important acid-catalyzed paraffin isomerization.

We conclude that Brønsted acidic properties play an important role in clay-catalyzed isomerization reactions. Also, clay selection, pretreatment, and activation procedures are important parameters in obtaining an optimum acidity. This does not seem to be fully recognized in the synthetic organic chemistry literature, where details on clay catalyst preparation, characterization, and activation are often lacking.

In addition, the present review indicates that to obtain H⁺-exchanged clay catalysts which combine a high thermal (~500°C) stability with a high Brønsted acidity, the negative charge on the clay layers should arise from isomorphous substitution in the tetrahedral sheets, such as is the case for beidellite. This results in active sites with acid strength comparable to those of zeolites. Therefore, clays may be advantageously used either in applications where zeolites are more expensive or in reactions of relatively large molecules that are unable to enter the zeolite pore structure.

REFERENCES


I. INTRODUCTION

Adsorption of a number of oxidizing agents on clays not only induces changes in their reactivity and selectivity but also simplifies commonly encountered workup and isolation problems associated with these reagents.

Foremost among the clay minerals used for this purpose has been the hydrous aluminosilicate—montmorillonite. Its adsorptive behavior toward small organic molecules (Theng, 1974) and organic polymers (Theng, 1979) has been described in some detail. The ability of montmorillonite to intercalate a large range of guest molecules (see Chapter 11) is related to its ability to undergo extensive expansion of its lamellar structure (Theng, 1979) as indicated in Fig. 1. The lamellae are composed of aluminosilicate sheets consisting of aluminium ions in an octahedral environment sandwiched between two layers of SiO₄ tetrahedra. In the naturally occurring clay the main interlayer cations are sodium and calcium; however, cation exchange can be effected by treatment with solutions of other ions such as Li⁺, Mg²⁺, Al³⁺, and NH₄⁺ (Theng, 1974). Isomorphous replacement of Al³⁺ ions by Mg²⁺ and Fe³⁺ and of Si⁴⁺ ions by Al³⁺ results in the layers carrying a permanent negative charge of 0.25–0.6 per formula unit. This charge is balanced by exchangeable counterions which, apart from those associated with the external clay surface, occupy the interlamellar regions.