Note

THE CATALYTIC PROPERTIES OF Vermiculite

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Vermiculites are widely occurring soil components related to mica and also to chlorite, and consist of silicate layers of complex formulas \((OH)_{x}Mg_{y}[Si, Al]_zO_{2z}\) separated from one another by water layers. The structure and physical properties of the mineral are described elsewhere. Large domestic deposits of vermiculite occur at Libby, Montana, and over a wide area near Greenville, South Carolina. The mineral has wide application as filler, absorbent, and especially as insulating material. It is also claimed to have some catalytic activity.

According to the patent literature, raw or treated vermiculite functions as catalyst for the isomerization of pinene, the polymerization of epoxy compounds, and the conversion of hydrocarbons. The information available is, however, rather meager and of little value. We have consequently made a series of exploratory experiments, principally using the raw mineral as catalyst for a variety of reactions, with the intent of surveying the catalytic properties of vermiculite.

Experimental Details

Vermiculite ore from Butte, Montana, was hand-sorted to remove detritus. The irregular, squarish flakes (about 10 x 10 x 2 mm) were ground in a ceramic ball mill. Particles below 40 mesh (U.S. Standard Sieve) were used in all reactions. The nitrogen B.E.T. surface area of the powder was 18.5 m²/g. A portion of the powder was slurried to a thick paste with an aqueous nickel nitrate solution. The volume and concentration of the impregnating solution were enough to yield a catalyst containing 7.0% nickel by weight. The paste was dried at room temperature and the resulting solid was heated for four hours in air at 500° to decompose the nitrate to oxide. The catalyst was reduced in situ in flowing hydrogen at 400° for one hour before use.

All analyses of reactants and products of the various reactions were made by
gas chromatography using standard techniques, with the exception of nitrobenzene hydrogenation. Aniline was detected by tests described by Mulliken and estimated indirectly by the amount of hydrogen consumed. All liquid reactants were of C.P. grade, and gases were Matheson and Coleman C.P. grade and were used without further purification. Analyses of the mineral are reported elsewhere.

Experiments, Results, and Evaluation

A variety of apparatus was used. Vapor-phase reactions were carried out with 12 ml. of catalyst in an atmospheric flow apparatus with a vertical furnace very similar to that of Komarewsky and Riesz. When used with reactants normally liquid at room temperature, the liquid was introduced with a syringe through a septum at a roughly constant rate of 1 ml/min. The liquid vaporized on the Pyrex preheated chips, and was then swept into the reaction zone. Liquid-phase hydrogenations were carried out with a vibration stirred apparatus. Pinene isomerization was carried out in a three-necked flask fitted with a mercury-seal stirrer, and isomerization of n-hexane in a rocking autoclave.

The results of the various test reactions are briefly summarized by Table I. As the intent of the investigation was exploratory, no attempt was made to determine optimum reaction conditions. Some of the experiments were repeated with the nickel-impregnated catalyst.

The acidity of the vermiculite powder was determined according to the method suggested by Thomas et al. Vermiculite was dried at 200° for three hours in air and was then slurried with water, and the mixture was subjected to filtration with NaOH. The acidity of vermiculite powder was 0.04 meq/g. This value is low in comparison to that of 0.41 meq/g found by Thomas et al. for a natural clay. The cracking activity of that clay was 43, on the basis of an arbitrary scale of 100 assigned to Superfiltrol (a commercial, clay-cracking catalyst).

The negative results of the cracking and isomerization reactions, which require the catalyst to have some acid character, are congruent with the low acidity that was found. Some methane, ethane, and propene were produced from butane, but this involved thermal rather than catalytic cracking. The same products were obtained under the same conditions over glass beads, although to a lesser extent, probably because the surface area of the beads was smaller than that of the vermiculite.

Some methane was formed from butane-hydrogen mixtures at 202°, and at 395° the amount of methane formed decreased and catalytic coke was formed. This may have been caused by chemisorption of butane at centers produced by a partial reduction of the surface by hydrogen. As propane or other products were not detected, this suggests that a simultaneous cracking and polymerization reaction
TABLE I. Reactions with Vermiculite Catalysts

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst (a)</th>
<th>Reactor (b)</th>
<th>Reaction Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumene cracking</td>
<td>RV</td>
<td>AFR</td>
<td>N₂ sweep gas: 60 ml/min; T: 285–400°.</td>
<td>No reaction below 400°; coke formation at 400°.</td>
</tr>
<tr>
<td>Butane cracking, dehydrogenation</td>
<td>RV</td>
<td>AFR</td>
<td>Butane: 40 ml/min; T: 200–500°.</td>
<td>No reaction up to 415°, but CH₄, C₂H₆, C₃H₆, and coke formation above 415° (thermal cracking at 470, 490°).</td>
</tr>
<tr>
<td>Hexane isomerization</td>
<td>RV</td>
<td>RA</td>
<td>H₂: psig; T: 125°; time: 1 hr; 4 g. catalyst; 10 g hexane.</td>
<td>No reaction.</td>
</tr>
<tr>
<td>α-Pinene isomerization</td>
<td>RV</td>
<td>3NF</td>
<td>T: 160°; time: 10 hr.; 4 g. catalyst; 50 g. α-pinene.</td>
<td>Product: α-pinene, 25%; camphene, 45%; monoterpenes, 30%.</td>
</tr>
<tr>
<td>Benzene hydrogenation</td>
<td>RV</td>
<td>AFR</td>
<td>H₂: 50 ml/min; T: 397°.</td>
<td>Only coke formed at 397°.</td>
</tr>
<tr>
<td>CO oxidation</td>
<td>RV</td>
<td>AFR</td>
<td>CO: 60 ml/min; O₂: 110 ml/min; T: 130–251°.</td>
<td>No reaction to 213°. 40% of CO converted to CO₂ at 251°.</td>
</tr>
<tr>
<td>Methyl linolenate hydrogenation</td>
<td>V-Ni</td>
<td>VSR</td>
<td>127° for 50 min; 40 mg catalyst; 492 g linolenate.</td>
<td>No reaction.</td>
</tr>
<tr>
<td>Cyclohexanol dehydration</td>
<td>RV</td>
<td>AFR</td>
<td>N₂ sweep gas: 75 ml/min; T: 179°.</td>
<td>30% conversion to cyclohexene.</td>
</tr>
</tbody>
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The Catalytic Properties of Vermiculite

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<tr>
<td>Cyclohexanol dehydration</td>
<td>RV</td>
<td>AFR</td>
<td>N₂ sweep gas: 75 ml/min, after heating catalyst to 500° for 2 hr in nitrogen.</td>
<td>20% conversion to cyclohexene at 209°. At 300° only coke is formed.</td>
</tr>
<tr>
<td>Nitrobenzene hydrogenation</td>
<td>RV</td>
<td>VSR</td>
<td>70°, for 5 hr; 40 mg catalyst; 6 g nitrobenzene.</td>
<td>No reaction.</td>
</tr>
<tr>
<td></td>
<td>V-Ni</td>
<td>VSR</td>
<td>70°, for 5 hr; 40 mg catalyst; 6 g nitrobenzene.</td>
<td>13% conversion to aniline.</td>
</tr>
</tbody>
</table>

(a): RV = raw vermiculite catalyst; V-Ni = nickel-impregnated vermiculite.  
(b): AFR = atmospheric flow reactor; RA = rocking autoclave; 3NF = three-necked flask reactor; VSR = vibration stirred reactor.

leading to coke had occurred. The decrease in the amount of methane could have been caused by a greater polymerization at the higher temperature, or by a change in active surface brought about by a change in catalyst structure.³⁵³

The relatively high conversion of α-pinene is surprising in view of the low total catalyst acidity. It has been claimed, however, that non acidic solids could catalyze this isomerization³³, so that sites of high acid strength may not be required for this reaction, possibly the strain produced in the molecule on adsorption being sufficient to induce isomerization. Alternately, relatively weak acid sites constituting the low acidity found may be responsible for the reaction.

Negative results were obtained with hydrogenation reactions, and cracking rather than dehydrogenation was observed with butane. Some activity for the oxidation of CO was found. Raw vermiculite exhibited some dehydration activity, a 30% conversion of cyclohexanol to cyclohexene being obtained. The decline in activity following a two-hour heat treatment at 500° in nitrogen could be tied to a structural change following dehydration of the mineral above 290°³⁵⁴, or to a loss of surface area.³³

The results of the survey show that, in general, raw vermiculite had little intrinsic catalytic activity. The surface was relatively inert. The nickel-impregnated vermiculite catalyst showed some hydrogenation activity, however, suggesting that the use of vermiculite as carrier or support for catalytically active materials is feasible. For that purpose, the very inertness of vermiculite may be a desirable feature, and suggests the use of raw or treated vermiculite as dispersant in cases where an interaction between the active component and the carrier is not desirable.
Acknowledgment

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References

8) V. I. KOMAREWSKY and C. H. RIESZ, Oil Gas J. 42, 901 (1943).