

Selective Friedel–Crafts Alkylation on a Vermiculite, a Highly Active Natural Clay Mineral with Lewis Acid Sites

Shin-ichi OKADA, Katsumi TANAKA,[†] Yasuhiro NAKADAIRA,*
and Naoya NAKAGAWA

Department of Chemistry, The University of Electro-Communications,
1-5-1 Chofu-gaoka, Chofu, Tokyo 182

[†]Department of Electronics-Engineering, The University of Electro-Communications,
1-5-1 Chofu-gaoka, Chofu, Tokyo 182

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Synopsis. Acid-catalyzed Friedel–Crafts alkylation reactions of *p*-methylbenzyl chloride with benzene were carried out on four unmodified natural clay minerals. Phenyl-*p*-tolylmethane was quickly and selectively formed in the presence of vermiculite. Although the specific surface area of vermiculite is smaller than those of the other clay minerals examined, such a characteristic property of vermiculite as a catalyst may be attributed to the absence of Brønsted acid sites and to the Lewis acid sites on the outer surface of vermiculite.

Recently, some clay minerals, especially modified montmorillonite, such as a metal oxide pillard montmorillonite, have received much attention as catalysts having an interlamellar space which acts as the binding sites of metal cations as well as a variety of compounds.^{1–7)} However, the catalytic activities of natural clay minerals, except for montmorillonite, have not been studied in detail.

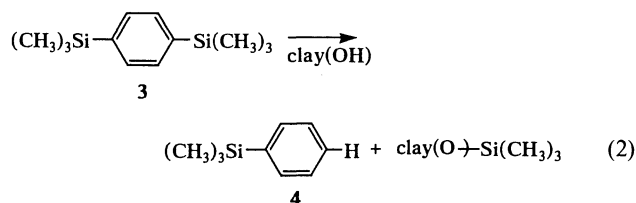
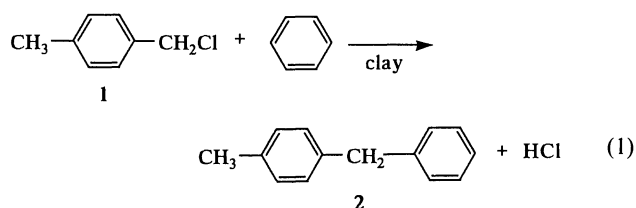
In the present paper we report on the properties of the active sites of some natural clay minerals for acid-catalyzed reactions and describe that despite the quite small surface area the natural vermiculite acts as a highly active catalyst for Friedel–Crafts alkylation, and gives a mono-alkylated product selectively.

Experimental

The clay minerals used in our experiments were protonated montmorillonite (hereafter denoted as H⁺-montmorillonite), tubular halloysite, vermiculite, and allophane, which had been mined in Niigata prefecture, Nagano prefecture in Japan,

Yunnan province, and Hebei province in China, respectively. The specific surface area and the elemental analysis as well as the crystal structures of the clay minerals employed are summarized in Table 1.

The reactions studied were the Friedel–Crafts alkylation of *p*-methylbenzyl chloride with benzene (Eq. 1) and Protodesilylation of 1,4-bis(trimethylsilyl)benzene (Eq. 2). After being



ball-milled in a stainless-steel pot, washed with distilled water and dried at 110 °C for 24 h, the clay sample (0.10 g for alkylation, 0.50 g for protodesilylation) was dispersed in benzene (50.0 g; 0.64 mol) in a 100 ml flask. After refluxing with stirring under Ar gas for 30 min, *p*-methylbenzyl chloride (0.04 mol) was added dropwise into the flask for the Friedel–Crafts

Table 1. Chemical Compositions of the Clay Minerals^{a)}

Sample name (Location)	Crystal type	Specific surface area ^{b)}	Elemental analysis ^{c)}						
		(m ² g ^{−1})	Si	Al	Fe	Ca	Mg	K	Na
H ⁺ -Montmorillonite (Niigata Pref., Japan)	2 : 1	102	100	23.8	2.8	1.9	4.1	0.3	0.6
Tubular halloysite (Yunnan Prov., China)	1 : 1	37.6	100	97.9	1.8	<0.1	0.5	0.7	<0.1
Vermiculite (Hevei Prov., China)	2 : 1	1.57	100	43.5	41.5	3.1	27.2	18.2	0.5
Allophane (Nagano Pref., Japan)	Amorphous	279	100	114.7	5.7	0.6	0.1	0.8	1.5

a) Clay samples were identified by differential thermal analysis and X-ray diffraction pattern (X-ray diffraction peaks: 15.6 Å (H⁺-montmorillonite), 10.0 and 7.3 Å (tubular halloysite), 10.0 Å (vermiculite), no peak (allophane). b) Measured BET adsorption method (N₂ gas). c) Obtained by classical gravimetric analysis (wet) including flame photometric analysis for sodium and potassium. The number of Si atoms is normalized to 100, and the other is referred to Si.

alkylation reaction. For protodesilylation, however, 1,4-bis(trimethylsilyl)benzene (0.002 mol) in benzene (10.0 g) was dropped into the flask. An aliquot (0.5 ml) of the reaction mixture was sampled at suitable time intervals. After centrifuging at 4000 rpm for 10 min, the products were analyzed and identified by means of gas chromatography (GC), GC mass spectroscopy (MS), and ^1H NMR spectroscopy. Quantitative analyses of phenyl-*p*-tolylmethane, poly-alkylated products, and (trimethylsilyl)benzene were carried out by a combination of GC and ^1H NMR spectroscopic methods.

For infrared (IR) analysis, a tablet of a clay sample (diameter of 9 mm, thickness of <0.1 mm) was set in an IR cell connected to a vacuum line. After being evacuated to 8×10^{-5} Torr, and heated at 100°C for 24 h, the tablet was exposed to the saturated pyridine vapor introduced in the cell chamber at room temperature for 1 min. After being maintained at 20°C for 1 h in order to attain adsorption equilibrium, the tablet was evacuated at 90°C for 8 h to remove any weakly adsorbed pyridine. After the sample was cooled to ambient temperature, the IR spectrum of the tablet was recorded in an absorption mode with a Perkin-Elmer 1600 series FTIR spectrometer.

Results and Discussion

The catalytic activities of the unmodified natural clay minerals listed in Table 1 were examined for the Friedel-Crafts alkylation of benzene with *p*-methylbenzyl chloride (**1**) under benzene refluxing conditions. The time profile of the alkylation is shown by a plot of the yield of phenyl-*p*-tolylmethane (**2**) vs. the reaction time (Fig. 1). Under these reaction conditions, reactant **1** was completely consumed within 30 min in the presence of vermiculite, H^+ -montmorillonite, and tubular halloysite. Figure 1 shows that the catalytic activity based on the yield of **2** was apparently in the order vermiculite $>$ H^+ -montmorillonite $>$ tubular halloysite $>$ allophane. Although monoalkylated **2** can possibly be more reactive under alkylation conditions, **1** is noted to be converted quantitatively to **2** in the presence of

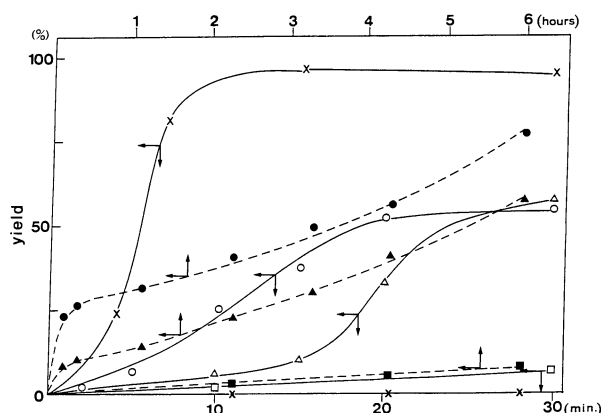


Fig. 1. Progress of the clay mineral catalyzed Friedel-Crafts alkylation of benzene with *p*-methylbenzyl chloride (**1**) (Eq. 1, solid lines), and that of the clay mineral catalyzed protodesilylation of 1,4-bis(trimethylsilyl)benzene (**3**) (Eq. 2, dotted lines).

The yield on the vertical axis represents for that of phenyl-*p*-tolylmethane for Eq. 1, and of (trimethylsilyl)benzene for Eq. 2, respectively.

○ and ● = H^+ -montmorillonite; △ and ▲ = tubular halloysite; × = vermiculite; □ and ■ = allophane.

vermiculite. Several increments of the amount of vermiculite still led to selective the formation of **2**. On the other hand, in the presence of H^+ -montmorillonite and tubular halloysite, although **1** was completely consumed, **2** was formed only in about 50% yield. In accord with these results, GC-MS and ^1H NMR of the reaction mixture showed that appreciable amounts of 1,4-bis(*p*-tolylmethyl)benzene and its isomer were formed together with **2**.

To classify the acid character of the active sites on clay minerals by means of IR spectroscopy, a pyridine adsorption experiment was conducted. The IR spectra of the pyridine adsorbed on H^+ -montmorillonite (a), tubular halloysite (b), and vermiculite (c) are shown in Fig. 2. The peaks at 1540 and 1450 cm^{-1} were assigned to those of the pyridinium ion and pyridine coordinated to the Lewis acid site, respectively.⁸⁾ Pyridinium ion is formed by the reaction of pyridine adsorbed with the Brønsted acid site. These spectra show that although both Brønsted and Lewis acid sites should exist on the surface of H^+ -montmorillonite and tubular halloysite, only Lewis acid sites are present on the surface of vermiculite. Figure 2 shows that the peak due to the acid sites on H^+ -montmorillonite and tubular halloysite is ten-times as intense as that on vermiculite. This accords with the small specific surface area of the vermiculite ($20\text{ m}^2/\text{g}^{-1}$).

Although Friedel-Crafts alkylation proceeds both on Brønsted and Lewis acid sites,⁹⁾ the protodesilylation of a phenylsilane can conceivably be brought about only by Brønsted acid sites.¹⁰⁾ In this sense, the protodesilylation of silylated benzene, such as 1,4-bis(trimethylsilyl)benzene (**3**), should be useful to examine the properties of the acid sites of clay minerals. As shown

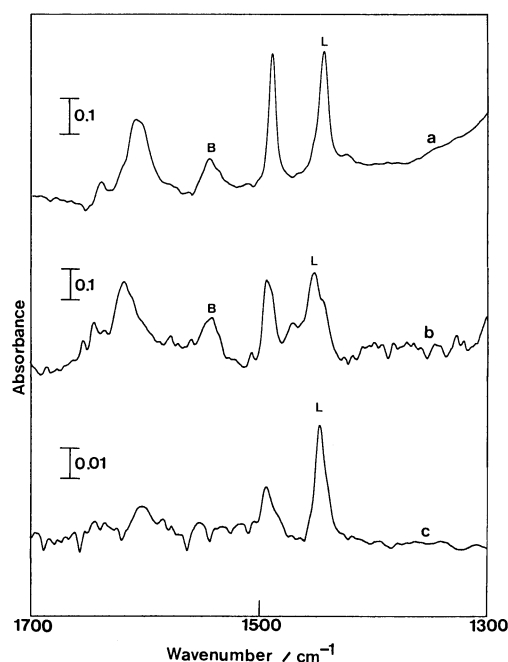


Fig. 2. Infrared spectra of pyridine adsorbed clay minerals.

a = H^+ -montmorillonite; b = tubular halloysite; c = vermiculite.

in Eq. 2, 3 reacts with a proton donor to yield (trimethylsilyl)benzene (4), and one of the trimethylsilyl groups is probably transferred to the oxygen of the hydroxyl group on the surface of clay minerals. In fact, the clay catalyst recovered after protodesilylation no longer showed any activity for protodesilylation. The protodesilylation reactions on some clay minerals were examined, and are illustrated in Fig. 1. This shows that H^+ -montmorillonite and tubular halloysite can protonate 3, and these two clay minerals act as Brønsted acid catalysts. However, protodesilylation did not occur on vermiculite. This is in accord with the fact that in the pyridine experiment described above, there was observed no IR band assignable to that due to a pyridinium ion.

It is noteworthy that on vermiculite 1 is selectively converted to the mono-alkylated product 2 in the Friedel-Crafts alkylation, and that no Brønsted acid site was clearly detected on its surface by an IR measurement, as described above.

Inspection of the chemical compositions of these clay minerals in Table 1 reveals that one of the important characteristics of vermiculite is the high content of iron; this may partly contribute to the activity and selectivity of the alkylation. In fact, vermiculite containing a much smaller amount of iron shows a lower activity than does the H^+ -montmorillonite for alkylation.^{11,12)}

The interlayer distance of the vermiculite is 0.4 Å according to X-ray diffraction; it did not change during the reaction. This result implies that the interlayer is too narrow to accommodate reactants. On vermiculite, the alkylating agent, *p*-methylbenzyl chloride, can be assumed to be activated by means of adsorption on the proper position to the Lewis acid center, and to react with benzene to form the corresponding cyclohexadienyl cation which yields 2 after deprotonation. However, the large substituent introduced may cause 2 to first approach and then react with the alkylating agent adsorbed on the active center; this prevents any further alkylation of 2. In conclusion, the high activity for Friedel-Crafts alkylation on vermiculite is induced by

the Lewis acid sites, probably Fe cations, in spite of the quite small specific surface area, while the specific selectivity for the reaction is interpreted as being due to an adsorption hindrance of the alkylated product 2.

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