

## SYNTHESIS OF METHYL-t-BUTYL ETHER FROM METHANOL AND ISOBUTENE USING A CLAY CATALYST

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**Abstract**—The acid-catalyzed reaction between methanol and isobutene to give methyl-t-butyl ether may be carried out using a cation-exchanged smectite as the catalyst. In 1,4-dioxan solvent at 60°C smectites exchanged with  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , or  $\text{Cr}^{3+}$  give yields of ~60% after 4 hr, whereas smectites exchanged with  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Na}^{+}$  give less than ~8% yield. The reaction is efficient only when certain solvents are used, e.g., with  $\text{Al}^{3+}$ -smectite the yield is ~5% when using 1,2-dimethoxyethane, diethyleneglycol diethylether, n-pentane, tetrahydropyran, N-methylmorpholine, or tetrahydrofuran solvents compared with ~60% using 1,4-dioxan solvent (4 hr). Moreover, the effective solvents depend somewhat on the clay interlayer cation. The use of tetrahydrofuran and tetrahydropyran gives ~35% yields at 60°C (4 hr) with  $\text{Fe}^{3+}$ - or  $\text{Cr}^{3+}$ -smectites but ~4% yield with  $\text{Al}^{3+}$ -smectite.

**Key Words**—Catalysis, Methyl-t-butyl ether, Smectite.

### INTRODUCTION

Smectitic phyllosilicates are well known for their activity in promoting acid-catalyzed reactions, such as dimerization and polymerization of unsaturated hydrocarbons (Hojabri, 1971; Solomon and Rosser, 1965). They are also capable of synthesizing ethers from alk-1-enes and the interlayer water naturally present in the clay (Adams *et al.*, 1979). Such ether products are thought to be derived from intermediate alcohols formed by the acid-catalyzed addition of water to the double bond of an alkene molecule. The protons necessary for the catalysis are provided by interlayer water which has greater acidity than free water (Fripiat *et al.*, 1964). These alcohol intermediates then react with further alk-1-ene molecules present in the interlayer region to form an ether. If this postulate of an alcohol intermediate is correct, it should be possible to synthesize ethers from alcohols and alkenes using the smectite clay as the necessary acid catalyst.

Recently, reactions between methanol and some alkenes were examined in this laboratory. Isobutene and methanol react when n-pentane is used as a solvent at 90°C in a closed vessel to give a large yield of methyl-t-butyl ether (MTBE) and minor amounts of t-butanol (Bylina *et al.*, 1980). In addition, variable but small amounts of 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene were produced. All of these products were formed via acid-catalyzed reactions (Figure 1).

The present work is an extension of this preliminary study (Bylina *et al.*, 1980) and examines the effect of varying the interlayer cation, the solvent, and the temperature on the yield of MTBE and other products. Csikos *et al.* (1975) and Watanabe *et al.* (1973) recently demonstrated that MTBE mixtures can increase the octane rating of gasoline, thus making the fuel more efficient and hence, more economical. Addition of

MTBE/alcohol mixtures to gasoline also allows the use of smaller amounts of lead alkyl compounds as anti-knock agents while increasing the efficiency of the fuel (Radchenko *et al.*, 1976). Moreover, the amount of carbon monoxide, nitrous oxides, and lead oxides released into the atmosphere on combustion of the fuel is greatly reduced (Nishizawa *et al.*, 1974).

### EXPERIMENTAL

The Wyoming bentonite used in this study (Volclay, foundry grade, purchased from Hopkin and Williams Ltd.) was crushed, separated from impurities, and size graded in a cyclone before delivery. Approximately 85% of the particles were specified as being <75  $\mu\text{m}$ . The silica and other impurities in this material were removed, and the <2- $\mu\text{m}$  clay fraction was selected by sedimenting the clay from a clay/water suspension. Cation exchange was effected by exposing the clay to salt solutions between 0.6 and 1 mole/liter for 24 hr. The clays were then centrifuged, resuspended in deionized water, and washed several times with deionized water until a test for the exchanging salt anion proved negative. The clay was then isolated by centrifugation, dried in an oven at 40°C, and ground finely using a pestle and mortar.

The pH of the exchanging salt solutions was measured (Table 1). At low pH considerable breakdown or leaching of the clay structure can occur which results in an increase in the surface area of the clay. In addition,  $\text{Al}^{3+}$  ions are released from the clay layers into the interlayer regions with the subsequent displacement of the interlayer cations. Control experiments were therefore carried out using a Na-exchanged clay which had been treated with HCl at pH 1 for 24 hr and then washed clean several times with deionized water. Portions of this control clay were also reexchanged with Na and

Cu(II) salts. The dried, exchanged clays were also examined thermogravimetrically in order to measure the amount of interlayer water present and to check that all excess exchanging salt had been removed.

The cation-exchange capacity (CEC) of a Cu(II)-exchanged sample and of an acid-treated Na-clay which had been subsequently reexchanged with Cu was determined. The powdered clay was fused in molten NaOH and then neutralized with HCl (Bennett and Reed, 1971). The analysis for copper was by precipitation of  $\text{Cu}(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_2$ . The CEC of the clay before acid washing was  $71 \pm 2$  meq/100 g, whereas that of the acid-treated clay was  $66 \pm 2$  meq/100 g of air-dried material.

The amount of interlayer water in the clay at the onset of a reaction can critically control the rate of the reaction and yield of the products (Adams *et al.*, 1979). Thus, a known and constant water content of the clay was desirable and was obtained by equilibrating preweighed amounts of clay over a saturated LiCl solution at 30°C for 48 hr. The atmosphere above this solution had a relative humidity of 12%. By thermogravimetry, an  $\text{Al}^{3+}$ -clay equilibrated under these conditions was found to contain  $4.5 \times 10^{-3}$  mole  $\text{H}_2\text{O}/\text{g}$  of clay.

The solvents and reactants were supplied by British Drug Houses or Aldrich Chemical Company. The solvents used were dried over a molecular sieve before use. Three commercially available catalysts derived from smectitic phyllosilicates (Süd-Chemie AG) were also examined (K10, KSF, and K306).

The reactions were carried out in Teflon-lined brass vessels fitted with a gas inlet valve and sampling port and containing a magnetic stirrer. Most reactions were carried out using 1.0 g of clay (preequilibrated at 12% RH) with 1  $\text{cm}^3$  of methanol, 3  $\text{cm}^3$  of solvent, and variable amounts (usually  $\sim 1.4$  g) of isobutene. The cells were loaded initially with the clay, solvent, and methanol and were then closed. Subsequently they were cooled to between  $-7^\circ\text{C}$  and  $-12^\circ\text{C}$ , and the isobutene was added via the gas inlet valve with constant shaking of the cell. The reaction mixture was heated with stirring usually for 4 hr. The cells were then cooled to  $-12^\circ\text{C}$  and the valves opened to allow any unreacted gas to escape. In certain runs the cell was chilled in liquid nitrogen, and the contents were transferred to a glass vessel fitted with a septum and allowed to warm to room temperature. The volatile products were removed via a double-ended needle into a nuclear magnetic resonance (NMR) sample tube containing carbon tetrachloride and tetramethylsilane and cooled to  $-70^\circ\text{C}$ . The tube was sealed and the NMR spectrum of the contents recorded in the usual way. The cells were then allowed to warm slowly to room temperature, and quantitative analyses of the products were carried out using gas liquid chromatography (GLC) with acetone as an internal standard. The MTBE used for the calibration was obtained by the Williamson ether synthesis

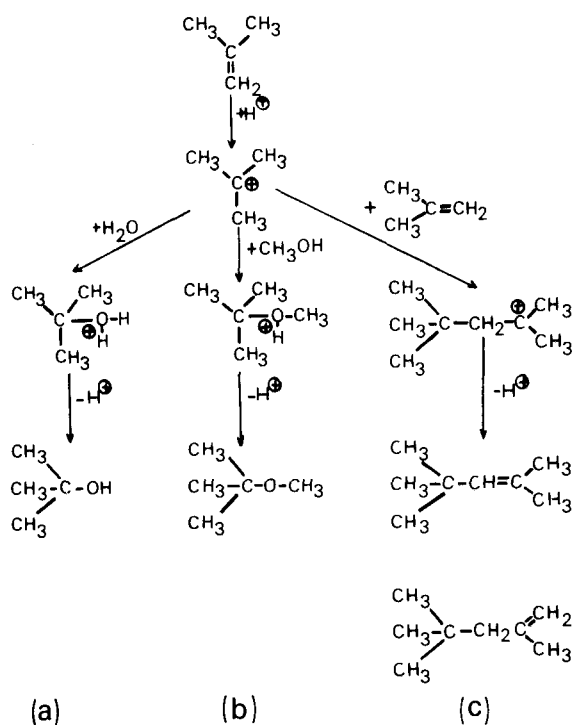


Figure 1. Mechanism of the production of (a) *t*-butanol, (b) methyl *t*-butyl ether, and (c) 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene.

by the reaction of iodomethane and potassium *t*-butoxide.

The detector sensitivity was determined for all the products and reactants on a Pye 204 chromatograph using a 5.7-m glass column of 0.25 inch i.d. packed with 3% (w/w) polyethylene glycol (PEG 20M) plus silver nitrate on Chromosorb G. This column was used to measure the amount of MTBE, 2,4,4-trimethylpent-1-ene, and 2,4,4-trimethylpent-2-ene, and the *t*-butanol and unused methanol present were determined on a 10-m,  $\frac{1}{8}$  inch i.d., stainless steel column packed with PEG 1540 plus silver nitrate on Chromosorb G.

Table 1. Source of exchanging cations and pH of exchanging solution.

Cation	Exchanging salt	Concentration of exchanging solutions (M)	pH of exchanging solution
$\text{Cu}^{2+}$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1	3.45
$\text{Fe}^{3+}$	$\text{FeCl}_3$	0.65	1.1
$\text{Al}^{3+}$	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.62	2.2
$\text{Cr}^{3+}$	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.75	0.8
$\text{Pb}^{2+}$	$\text{Pb}(\text{NO}_3)_2$	0.75	2.7
$\text{Ni}^{2+}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.86	3.9
$\text{Co}^{2+}$	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.74	4.4
$\text{Ca}^{2+}$	$\text{Ca}(\text{NO}_3)_2$	1	5.5
$\text{Na}^+$	$\text{NaCl}$	1	8.1

Table 2. Comparison of MTBE production using a variety of clay catalysts.<sup>1</sup>

Interlayer cation	Isobutene		MTBE yield <sup>2</sup> (mmole)	t-BuOH yield <sup>2</sup> (mmole)
	weight (g)	(mmole)		
Cr <sup>3+</sup>	1.3	23.2	14.5	1.12
Al <sup>3+</sup>	1.35	24.1	14.6	2.3
Fe <sup>3+</sup>	1.1	19.6	12.8	1.53
Cu <sup>2+</sup>	1.1	19.6	2.20	1.50
Pb <sup>2+</sup>	1.15	20.5	—	—
Ni <sup>2+</sup>	3.15	56.2	—	0.14
Co <sup>2+</sup>	1.6	28.5	—	0.2
Ca <sup>2+</sup>	1.15	20.5	—	—
Na <sup>+</sup>	1.45	25.9	0.48	0.18
Na <sup>+</sup> -clay acid treated at pH 1	1.25	22.3	14.0	0.3
Na <sup>+</sup> -clay acid treated at pH 1 and exchanged for Na <sup>+</sup>	1.1	19.6	0.1	0.5
Na <sup>+</sup> -clay acid treated at pH 1 followed by Na <sup>+</sup> exchange and then Cu <sup>2+</sup> exchange	2.25	40.1	2.0	2.3
DABCO	2.0	35.7	—	—
K10 catalyst	1.1	19.6	11.4	1.58
K306 catalyst	1.3	23.2	0.19	—
KSF catalyst	1.0	17.8	9.5	2.3

<sup>1</sup> Reaction = 1 g clay 12% RH + 1 cm<sup>3</sup> MeOH + 3 cm<sup>3</sup> 1,4-dioxan + isobutene  $\xrightarrow[60^{\circ}\text{C}]{4\text{ hr}}$  (25 mmole)

<sup>2</sup> — signifies negligible production.

The products detected by GLC were identified by comparison of retention times with standard samples. The MTBE could be isolated by distillation; GLC showed the presence of a contaminant, but the NMR spectrum indicated that the product was substantially pure. The mass spectrum was also recorded (gas chromatographic/mass spectral analysis on a 2.7-m column packed with PEG 20M and silver nitrate, which was coupled to an AEI MS-30 mass spectrometer and a DS50S Data System), and this too indicated the presence of a contaminant.

## RESULTS AND DISCUSSION

The reaction between isobutene and methanol was studied using clays with different interlamellar cations, a variety of acid-treated clays, and three commercially available acid-treated clay catalysts (K10, KSF, and K306). The conditions of the reactions were: 1 g clay (12% RH) + 1 cm<sup>3</sup> MeOH + 3 cm<sup>3</sup> 1,4-dioxan + 1.1–3.2 g isobutene, 4 hr at 60°C.

Yields of greater than 50% (Table 2) MTBE were obtained where the interlamellar cation was Fe<sup>3+</sup>, Cr<sup>3+</sup>, or Al<sup>3+</sup>. The clays which had been exchanged with monovalent or divalent cations gave low yields in comparison with clays exchanged with trivalent ions. This is probably due to the fact that trivalent cations have a greater polarizing power than monovalent and divalent cations. It is well known that the acidity of inter-

layer water is very dependent upon the polarizing power of the interlamellar cation (Mortland and Raman, 1968). The yields of MTBE using Cu<sup>2+</sup>-clays are greater than those for other divalent cations. Adams *et al.* (1979) found Cu<sup>2+</sup>-clays to be good catalysts for the addition of the elements of water to alk-1-enes to form alcohols and then ethers.

Yields of greater than 50% were also obtained using the industrial catalysts K10 and KSF and an acid-treated Na-clay. The K10 and KSF catalysts are acid-treated smectitic clays which probably have Al<sup>3+</sup> ions (leached from octahedral sites) as the interlayer cation, as does the acid-treated Na-clay that also gave a good yield of ether. The K306 catalyst, on the other hand, gave a poorer yield which is not surprising because this is a silica/alumina catalyst containing 85% silica (Hojabri, 1971). To test the hypothesis that the activity of the acid-treated clays was due to Al<sup>3+</sup>, a Na-clay that had been acid treated and reexchanged with Na (displacing any leached Al<sup>3+</sup>) gave only 0.1 mmole of MTBE as compared with 14 mmole produced by the clay that had been acid treated but that had not been subsequently reexchanged.

The yield of t-butanol in each reaction was less than the maximum amount possible from the thermogravimetric estimation of interlayer water initially present in the clay (4–4.5 mmole of t-butanol). The cation-exchanged clays which were efficient for MTBE synthesis

were generally the most efficient at producing t-butanol (although  $\text{Cu}^{2+}$ -clays gave larger yields of alcohol than would have been expected). It should be noted that more water may be available for reaction than that derived from interlayer water because some will invariably be present in the solvents and reactants. Another potential source of water is the acid-catalyzed reaction between two methanol molecules to give dimethyl ether (boiling point  $-26^\circ\text{C}$ ) and water. The products were not routinely analyzed for dimethyl ether, but the volatile constituents from a few selected runs were trapped and analyzed by NMR spectroscopy; in all cases small amounts of dimethyl ether were found. In no reaction did the amount of t-butanol exceed 4 mmole when a considerable excess of isobutene was present.

The experiments described above differed from previous studies in that dioxan was used as a solvent. Previously only alkane solvents were used to avoid preferential intercalation of solvent molecules resulting in a blocking of active sites. However, as the present data indicate, such blocking does not occur and, indeed, it was possible to produce MTBE at  $60^\circ\text{C}$ , whereas previously (Bylina *et al.*, 1980) temperatures of  $95\text{--}100^\circ\text{C}$  were required. At  $60^\circ\text{C}$  the use of n-pentane as solvent gave only 0.28 mmole MTBE with an  $\text{Al}^{3+}$ -clay. Therefore, the range of solvents was extended to include 1,4-dioxan, n-pentane, diethylene glycol diethyl ether, tetrahydropyran, N-methylmorpholine, tetrahydrofuran, and 1,2-dimethoxyethane.

The basal spacings of the exchanged clays (Table 3) show that all of the above solvents penetrate between the clay layers. For  $\text{Cu}^{2+}$ - and  $\text{Al}^{3+}$ -exchanged clays, only 1,4-dioxan was an effective solvent (Table 4) although, of course, the  $\text{Al}^{3+}$ -clay is much more effective than the  $\text{Cu}^{2+}$ -clay. For  $\text{Fe}^{3+}$ - and  $\text{Cr}^{3+}$ -clays tetrahydropyran and tetrahydrofuran were also effective, and in general these two clays gave better results than  $\text{Al}^{3+}$ - and  $\text{Cu}^{2+}$ -clays with all solvents except 1,4-dioxan. This dependence of yield on the solvent employed and the apparently highly specific solvent-interlayer cation relationships observed are totally novel features of clay catalysis. The X-ray powder diffraction data (Table 3) show that the two solvents which give the largest interlayer spacings give the lowest yields (apart from

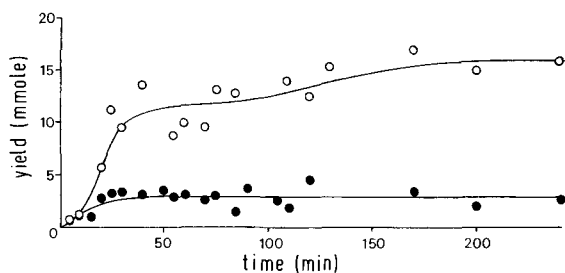


Figure 2. Yield of methyl t-butyl ether (○) and t-butanol (●) as a function of time.

N-methylmorpholine). Hence the solvent effect cannot be due to a variation in the ease with which the reaction reaches the active sites. The solvent has a role to play in determining the distribution of reactants and products both in the interlayer region and outside the clay. However, miscibility cannot be the sole explanation of the effects observed because the solvent effects are dependent upon the identity of the interlayer cation. Specific interactions between the interlayer cations and the solvent could also be significant and may well explain the negligible yields when using N-methylmorpholine. This material is bound more tightly to the interlamellar cations than any likely reactant, thus suppressing reaction. Indeed, a  $\text{Cu}^{2+}$ -clay changed color from pale blue-green to dark green on adding N-methylmorpholine. This coloration was not seen with other solvents and is due to coordination via the N atom.

The other solvents probably fill the coordination sphere of these cations, and the degree of interaction between the solvent molecule and the interlayer cations depends on the polarizing power of the latter. The relevant radii are  $\text{Cu}^{2+} = 0.72 \text{ \AA}$ ,  $\text{Fe}^{3+} = 0.64 \text{ \AA}$ ,  $\text{Cr}^{3+} = 0.64 \text{ \AA}$ , and  $\text{Al}^{3+} = 0.53 \text{ \AA}$ . Thus,  $\text{Al}^{3+}$  will interact most strongly with the solvent molecules, a feature which should, presumably, be unfavorable for reaction. However, a high charge : radius ratio is also required to polarize the alkene double bond readily so as to enhance reaction. For reactant molecules to have access to the active sites they must displace solvent molecules from

Table 3. Basal spacings of various cation-exchanged clays intercalated with various solvents.

Solvents to be intercalated	$\text{Al}^{3+}$ -clay (Å)	$\text{Fe}^{3+}$ -clay (Å)	$\text{Cu}^{2+}$ -clay (Å)	$\text{Cr}^{3+}$ -clay (Å)
1,4-dioxan	14.85	14.73	14.96	15.09
n-pentane	14.60	14.48	13.69–13.98	14.71
tetrahydrofuran	14.25	14.24	14.35	17.31
1,2-dimethoxyethane	16.83	16.83	16.97	17.65
diethylene glycol diethylether	18.03	18.6	18.58	18.20
tetrahydropyran	15.22	15.35	15.10	15.09
N-methylmorpholine	14.96	14.96	14.96	14.96
No solvent; clay air dry (for comparison)	14.14	13.59	12.10	15.09

Table 4. Variation of yield of MTBE when using different solvents.<sup>1</sup>

Solvent	Al <sup>3+</sup> -clay		Fe <sup>3+</sup> -clay		Cr <sup>3+</sup> -clay		Cu <sup>2+</sup> -clay	
	isobutene (mmole)	MTBE (mmole)	isobutene (mmole)	MTBE (mmole)	isobutene (mmole)	MTBE (mmole)	isobutene (mmole)	MTBE (mmole)
1,2-dimethoxyethane	20.5	0.65	23	8.6	20	3.32	—	—
diethyleneglycoldiethylether	17.8	0.31	31	7	39	4.3	—	—
n-pentane	58	0.28	3	8	80	6.6	87.5	0.037
tetrahydropyran	23.2	1	14.2	5	39.2	16.5	60.7	0.135
N-methylmorpholine	41	0.2	37.5	0.2	30	—	39.2	—
tetrahydrofuran	28	0.2	55	17.3	60	16.9	—	—
1,4-dioxan	24.1	14.6	19.6	12.8	23.2	14.5	19.6	2.20

<sup>1</sup> The isobutene value quoted is the number of mmole of isobutene initially present. The MTBE value is the number of mmole of MTBE produced.



the coordination sphere of the cation. With Fe<sup>3+</sup> or Cr<sup>3+</sup> the interaction is slightly weaker than for Al<sup>3+</sup>, and consequently exchange of reactant molecules for solvent, and hence reaction, should occur more easily.

However, none of these possibilities taken by itself adequately accounts for the specific solvent/cation pairings which have been observed to modify the efficiency of the reaction. The reaction rate depends on a number of equilibria involving the distribution of methanol and isobutene between clay and external solution, and possibly on other equilibria controlling the distribution of these molecules between active sites in the clay and the remaining interlayer space. These equilibria are obviously sensitive to the presence of unreactive solvent molecules which could modify the concentrations of participating molecules within the interlayer space and themselves be competitors for coordination at active sites. Of course, much has been discovered regarding selective adsorption of specific adsorbates onto clays (see e.g., Brindley and Ruston, 1958; Doehler and Young, 1962; Dowdy and Mortland, 1967; Heydemann and Brindley, 1968; Espinasse and Siffert, 1979). The present results indicate that cation/solvent interactions can affect the competition between solvent, water, reactant and reaction products for sites in the solvation shell of the active cations and in this way modify dramatically the catalytic efficiency of the clay.

Using n-pentane as solvent, temperatures of 90°C were requisite for MTBE production; at these temperatures some dimers of isobutene were observed in the products even without an excess of isobutene. However, at the lower temperatures which were useful when using an ether-type solvent, significant production of dimers was not observed.

Reactions using Al<sup>3+</sup>-clays (1 g) with 1,4-dioxan (3 cm<sup>3</sup>) as solvent and 1 cm<sup>3</sup> of methanol and 1.4 g isobutene at 60°C were carried out and stopped after various times. A graph of MTBE and t-butanol yield vs. time (Figure 2) shows that the yield of MTBE increased and reached a steady value after about 2 hr, whereas

the t-butanol production was constant after about 30 min. The MTBE production curve is not a single smooth process due possibly to the MTBE production being linked in some way to the production of t-butanol. The synthesis of t-butanol involves the removal of the interlayer water which is also responsible for the provision of the protons which make the interlayer regions so acidic. From thermogravimetric data each gram of the Al<sup>3+</sup>-clay catalyst contains 4.5 mmole of water, but after 30 min, 3.5–4.0 mmole of t-butanol were formed, leaving only 0.5 to 1.0 mmole of interlayer water to provide the acid medium. The remaining water was, however, sufficient for the catalyst to function satisfactorily.

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**Резюме**—Реакция с кислотой как катализатором между метанолом и изобутаном для получения метил-*t*-бутилового эфира может быть проведена, используя катионо-обменный смектит как катализатор. В 1,4-диоксановом растворителе при темп. 60°C количество смектитов, обмененных с  $Al^{3+}$ ,  $Fe^{3+}$ , либо  $Cr^{3+}$  было ~60% после 4 часов, в то время как количество смектитов, обмененных с  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Ca^{2+}$ , и  $Na^{+}$  было менее 8%. Реакция была эффективна только тогда, когда использовались определенные растворители. Так например, при использовании растворителей 1,2-диметоксиэтана, диэтиленгликолевого диэтилового эфира, *n*-пентана, тетрагидропирана, *N*-метилморфолина, или тетрагидрофурана количество  $Al^{3+}$ -обменного смектита было ~5% по сравнению с 60% при применении 1,4-диоксанового растворителя (4 часа). Кроме того эффективные растворители зависят в некоторой степени от межслойного катиона глины. Использование тетрагидрофурана и тетрагидропирана дает ~35% при 60°C (4 часа) с  $Fe^{3+}$  либо  $Cr^{3+}$ -смектитами, но только ~4% с  $Al^{3+}$ -смектитами. [E.C.]

**Resümee**—Die durch Säure katalysierte Reaktion zwischen Methanol und Isobutylen zu Methyl-*t*-Butyläther kann unter Verwendung eines Kationen-ausgetauschten Smektits als Katalysator durchgeführt werden. In einem 1,4-Dioxan als Lösungsmittel geben Smektite, die mit  $Al^{3+}$ ,  $Fe^{3+}$ , oder  $Cr^{3+}$  ausgetauscht worden sind, bei 60°C nach 4 Stunden eine Ausbeute von etwa 60%, während Smektite, die mit  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Ca^{2+}$ , und  $Na^{+}$  ausgetauscht wurden, weniger als etwa 8% Ausbeute ergeben. Die Reaktion ist nur wirksam, wenn gewisse Lösungsmittel verwendet werden; so beträgt unter Verwendung von  $Al^{3+}$ -Smektit die Ausbeute etwa 5%, wenn 1,2-Dimethoxyäthan, Diäthylenglykol-Diäthyläther, *n*-Pentan, Tetrahydrofuran, *N*-Methylmorpholin, oder Tetrahydrofuran als Lösungsmittel verwendet werden, während die Ausbeute etwa 60% beträgt, wenn 1,4-Dioxan als Lösungsmittel (4 Stunden) verwendet wird. Darüberhinaus hängt die Wirksamkeit des Lösungsmittels in gewisser Weise vom Zwischenschichtkation des Tons ab. Tetrahydrofuran und Tetrahydrofuran geben bei 60°C (4 Stunden) mit  $Fe^{3+}$ -oder  $Cr^{3+}$ -Smektit etwa 35% Ausbeute aber nur etwa 4% Ausbeute bei  $Al^{3+}$ -Smektit. [U.W.]

**Résumé**—La réaction catalysée par un acide, entre le méthanol et l'isobutène pour donner l'éther méthyl-*t*-butyl peut être produite en employant comme catalyseur une smectite à cations échangés. Dans un solvant dioxane-1,4 à 60°C, des smectites échangées à  $Al^{3+}$ ,  $Fe^{3+}$ , ou  $Cr^{3+}$  ont produit ~60% après 4 heures, tandis que des smectites échangées à  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Ca^{2+}$ , et  $Na^{+}$ , ont produit moins de ~8%. La réaction n'est efficace que lorsque certains solvants sont employés, par exemple, avec la smectite- $Al^{3+}$ , le produit est ~5% quand on emploie des solvants diméthoxyéthane-1,2, diéthyléther diéthylenglycol, pentane-*n*, tétrahydropyrane, méthylmorpholine-*N*, ou tétrahydrofurane comparé avec ~60% obtenus en employant le solvant dioxane-1,4 (4 heures). De plus, les solvants effectifs dépendent quelque peu du cation argile intercouche. L'emploi de tétrahydrofurane et de tétrahydropyrane produit ~35% à 60°C (4 heures) avec des smectites- $Fe^{3+}$  ou - $Cr^{3+}$ , mais ~4% avec la smectite- $Al^{3+}$ . [D.J.]