JOURNAL OF CATALYSIS 75, 190–195 (1982)

Conversion of 1-Hexene to Di-2-hexyl Ether Using a Cu^{2+}—Smectite Catalyst

Smectite clays have been extensively used as acid catalysts in the past (*1*) but it is only relatively recently that the use of cation-exchanged smectites has been investigated for the selective conversion of organic species to the desired products (*2*–*8*). One novel acid-catalysed reaction, that of hex-1-ene to di-2,2′-hexyl ether (ether), is noteworthy since it is the only case reported in which some part of the clay structure (the interlamellar water) is incorporated into the product. The clay is then, strictly, not a catalyst. A further point of interest is that this method appears to be the most efficient by far for producing such bis-secondary ethers.

It has previously been shown (*6*, *7*) that the yield of the ether produced by the reaction depends upon the interlayer cation in the clay and also upon the amount of water between the clay layers. A clay containing one layer of water molecules between the aluminosilicate sheets gives a total conversion of interlayer water in 5 h, whereas a clay with two interlamellar water layers gives about twice this yield but not until after perhaps 150 h. A clay with three interlamellar water layers, however, gives only a small ether yield even after over 200 h, probably because of miscibility problems.

In this study, we have examined more closely the case when the clay contains only a single interlamellar water layer. We have used a Cu^{2+}-exchanged clay as the catalyst since this was found (*7*) to be moderately active catalytically but produced very clean reactions.

EXPERIMENTAL

Clay Preparation and Characterization

The < 2 μm fraction of a bentonite (BDH) was collected by sedimentation and was exchanged with Cu^{2+} ions by immersing the solid in ~ 0.5 mol dm^{-3} $CuSO_4$ solution for 48 h. The clay was centrifuged and washed several times in deionised water to remove excess salt. For all experiments preweighed Cu–clay samples were equilibrated for 1–2 days over a saturated lithium chloride solution at 30°C which produced a relative humidity (rh) of 12%.

The clay has a cation exchange capacity (cec) of 70 meq/100 g of air-dry material, which corresponded to 0.25 Cu^{2+} per Si_8O_{20} unit. Thermogravimetric analysis showed that clay (12% rh) contained 7.5% water, i.e., we have 3.3 molecules of water per Si_8O_{20} unit—the clay formula is $(Mg, Fe, Al)_4Si_8O_{20}(OH)_4 \cdot 0.25\,Cu^{2+} \cdot 3.3\,H_2O$. For a clay which was air dry we obtained 3.7–4.0 water molecules per unit cell depending upon the atmospheric rh. After about 8 min in air the weight of a clay previously equilibrated at 12% rh increased by 1.5% (equivalent to 0.7 H_2O per cell).

X-Ray measurements on the Cu–clay (12% rh) and air-dry Cu–clay which were immersed in hex-1-ene at room temperature showed that in all cases hex-1-ene was intercalated; indeed the basal spacing increased from 12.4 to 13.2 Å for Cu–clay (12% rh) and 14.7 Å for air-dry Cu–clay. However, the peak profiles were extremely broad, suggesting poor ordering of interlamellar species and, in addition, at room

0021-9517/82/050190-06$02.00/0

temperature it appeared to take several days for the basal spacing to attain its maximum value. From thermogravimetric evidence it was apparent that between one and two hex-1-ene molecules per unit cell could be accommodated in the interlamellar space.

Analysis of Reaction Products

Gas–liquid chromatography (GLC) was used to monitor reactant purity, to follow the reaction, and to select the conditions for mass spectrometer measurements. The glass columns used were packed with either (a) 3% polyethylene glycol (PEG) 20M with or without $AgNO_3$ or (b) 3% PEG 400, which was especially good for separation of alcohols from dimers and ethers. The materials were supported on silanized Chromosorb G. Identification of reaction products was performed on a coupled GLC/mass spectrometer.

Reaction under Reflux Conditions

A charge consisting of hex-1-ene (2.5 cm^3), *n*-hexane (5 cm^3), and 0.5 g of Cu–clay (12% rh, containing 2.06 mmol H_2O) was boiled in a 50-cm^3 round-bottom flask with a Liebig condenser for 5 h. During the reflux period it was noticeable that water, originally present in the clay, was being removed as an azeotropic mixture, the quantity so removed being variable and dependent on the size of the flask and condenser used.

Reactions in a Closed System

A brass vessel with Teflon internal walls and with a septum sampling port was used for the reaction above the boiling point of hex-1-ene. The vessel was charged with hex-1-ene (7.5 g—no solvent was usually used) and 0.8–1.0 g Cu–clay (12% rh), a magnetic stirrer was added, and the vessel closed and placed in a water bath. The reaction progress was measured by GLC by removing samples with a microsyringe. Any addition of material to the reaction mixture could also be made using the microsyringe.

TABLE 1

Reaction of Hex-1-ene and Cu–clay

Conditions	Time (min)	Yield[a] (%)	
		Ether	Hexan-2-ol
Under reflux at 64°C			
In solution	300	81	1
In clay (extracted)	300	—	17
Closed system at 68°C			
In solution	360	5	—
In clay (extracted)	360	1	10
Closed system at 81°C			
In solution	345	24	23
In clay (extracted)	345	1	39

Note. Reactants: 0.5 g Cu–clay (12% rh) [0.623 mmol clay, 2.07 mmol H_2O] + 2.5 ml 1-hexene (19 mmol) + 5.0 ml solvent (*n*-hexane or *n*-octane/*n*-pentane mixtures).

[a] Based on the percentage of the original clay interlayer water consumed to form the appropriate product.

Recovery of Products from the Clay Interlayer Space

Since the distribution of reactants and products between the supernatant and the interlamellar space was unlikely to be uniform, 1.0 cm^3 of a 1 : 1 (v/v) mixture of methanol and *n*-pentane was added to the suspension. A single liquid phase was produced and it was considered that the methanol displaced most, if not all, of the interlamellar organic matter. Neglect of this procedure could lead to certain products being overlooked (Table 1).

RESULTS

Preliminary Reflux Reactions

Reflux runs were made to characterize the products of the reaction and to examine the distribution of the products between the liquid phase and the interlamellar space. *n*-Octane was used as an internal standard. During a 5-h reflux the weight of the reaction mixture decreased by 760 mg (~1.14

cm^3). The yield of the ether was ~80% of that possible if all of the water molecules initially present between the clay sheets were consumed. After addition of the extraction mixture some hexan-2-ol was found showing that this material is selectively held in the interlamellar space and not in the external reaction mixture. There is also evidence of a small amount of hexan-2-one which could arise from reaction of hexan-2-ol and atmospheric oxygen or by dehydrogenation of hexan-2-ol; it has been found previously that sheet silicates can catalyse oxidation and hydrogen exchange reactions (*3*, *4*).

A reflux reaction using large amounts of material (20 g Cu–clay (12% rh)) was used to produce the ether for standard solutions. After removal of the clay by filtration the reaction mixture was distilled under vacuum to separate the ether; this gave a material which contained 5% of hexene dimer impurities. This purity error was taken into account in all quantitative measurements. The mass spectrum of the ether corresponded to that previously reported (*6*). In particular the intense peaks at $m/e = 129$ (from $C_8H_{17}O^+$) and 85 (from $C_6H_{13}^+$) were observed. In one case a mass spectral peak was observed at $m/e = 143$. This would be a likely fragment ion ($C_4H_9CH(CH_3){-}O^+ = C_3H_6$) from 2-hexyl 3-hexyl ether, and it was possible that a little of that ether had also been formed.

Kinetics of the Ether Forming Reactions

A study was made of the reaction using the sealed reaction vessels which effectively stopped the loss of any of the reactants (including water) from the system. The variation of ether, hexan-2-ol, and hexan-3-ol were all followed with time (Fig. 1). For the ether we have two straight line regions with equations

(i) $\log(\text{yield}) = 9.869 \times 10^{-3}t - 2.0112$,

where t is in minutes and the yield is expressed as a fraction of the total interlayer water consumed.

(ii) $\log(\text{yield}) = -1.096 \times 10^{-4}t - 6.95 \times 10^{-2}$.

The first line indicates a pseudoautocatalytic process and the second shows a slow decomposition of the product. The linear relation of log (yield) with time may be an approximation to more complicated functions involving diffusion phenomena.

For hexan-2-ol we have a smooth increase in production until the ether production is complete; the amount of hexan-2-ol then remains roughly constant. For hexan-3-ol the yield curve follows the same trends shown by hexan-2-ol, but with a concentration one order of magnitude smaller. The fact that hexan-3-ol was detected at all supports the previous suggestion derived from the mass spectrum that there may be a little 2-hexyl 3-hexyl ether produced.

The mean value of ether production from 1 g Cu–clay (12% rh) was estimated to be 0.48 mmol/h, but from the region of 95% of the maximal reaction yield we have 4.20 mmol/h. The most significant feature of

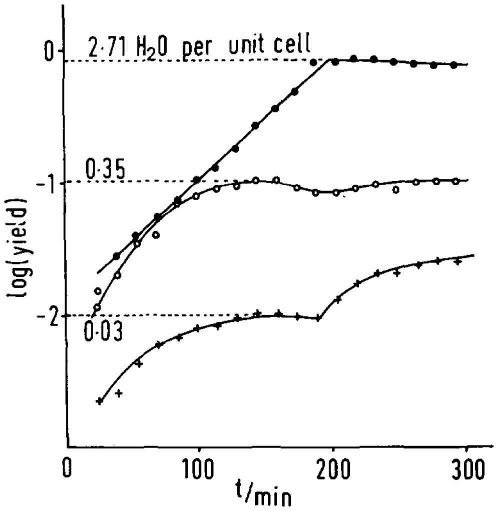

FIG. 1. Yield of di-2,2′-hexyl ether (●), hexan-2-ol (○), and hexan-3-ol (+) as a function of time for reactions carried out in a sealed reaction vessel at 100°C. One gram of Cu–clay (12% rh) and 7.5 cm^3 hex-1-ene were used. Yields are expressed in terms of the percentage usage of the interlamellar water initially present in the clay.

Fig. 1 is that at the point at which the sharp change occurs in ether production it is found that a total of 3.1 H_2O per unit cell have been used to produce the ether and hexan-2-ol observed in the external solution. The remaining ether and hexan-2-ol held in the clay interlayer region bring the total to 3.26 H_2O compared with 3.3 H_2O per cell which were originally present. It is considered that these quantities are essentially equal and that ether production continues until all of the available interlayer water is consumed. After this, other processes also catalysed by the clay, e.g., ether decomposition, hexene dimerisation, take over.

Effect of Addition of Hexan-2-ol during Reaction

The yield of hexan-2-ol appears to be related to ether production (Fig. 1). Moreover, it is possible to describe the ether formation (at least formally) as addition of water to hex-1-ene to give hexan-2-ol, followed by reaction of hexan-2-ol and a further hex-1-ene molecule to give ether. It was therefore decided to test the effect of addition of small amounts of hexan-2-ol during the reaction (Fig. 2).

Until the first hexan-2-ol injection, ether production occurs as before, but immediately after each hexan-2-ol injection the ether production was retarded and the hexan-2-ol was consumed by the clay. It can also be seen that at times >300 min when the number of water molecules remaining in the clay is small, the rate of consumption of the injected hexan-2-ol increases. Overall the multiple injections of hexan-2-ol increased the total yield of ether although the rate of production was decreased.

There appear to be several explanations for consumption of hexan-2-ol; reaction directly with hex-1-ene to produce ether could occur, or dehydration to hex-1-ene, together with water, and subsequent production of ether. Again a bimolecular reaction ($2ROH \rightarrow ROR + H_2O$) might be possible. However, none of these possibilities seems to accord with our observations, for the disappearance of hexan-2-ol is not mirrored directly by increased ether production, while dehydration would not be expected to lead exclusively to hex-1-ene, but rather to yield a substantial proportion of hex-2-ene. Other experiments have shown that not merely is hex-2-ene not converted to ether but its introduction into a reacting system can suppress the reaction of hex-1-ene.

The presence of hexan-2-ol in the reac-

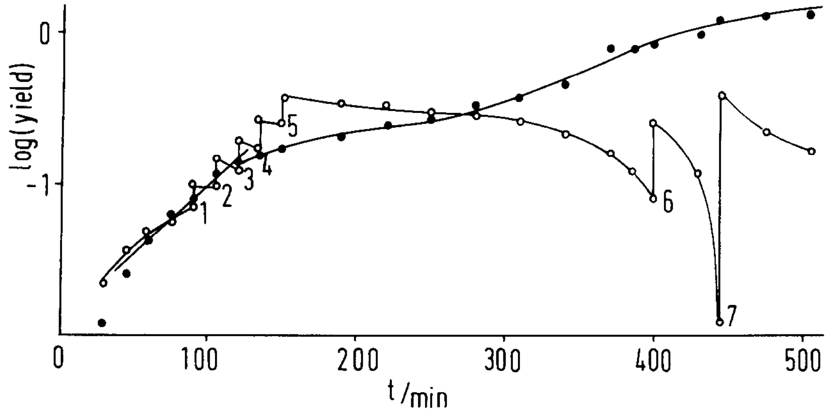

FIG. 2. Yield of di-2,2′-hexyl ether (●) as a function of time. During this reaction injections of hexan-2-ol (○) were made: (1) 10 μl, (2) 10 μl, (3) 10 μl, (4) 10μl, (5) 10 μl, (6) 20 μl, (7) 80 μl. The reaction was carried out at 100°C in a sealed vessel using 1 g Cu–clay (12% rh) and 7.5 cm^3 hex-1-ene.

tion mixture could affect the transport of hex-1-ene and water in the clay interlayer space and also the distribution between this space and external solution. In addition there is also the possibility of competition between the different chemical species for coordination to the exchangeable cations in the clay. At present, not much is known of these effects in clays.

Effect of Water Addition

Since ether production appears to cease when all of the original interlamellar water has been consumed it was decided to investigate whether the catalyst could be regenerated, or its life extended, by addition of water, either before or after the point at which ether production ceased. However, the water was not used to produce more ether, but instead there was an increase in hexan-2-ol and hexan-3-ol production. It is probable, of course, that after a considerably longer time this extra hexanol might lead to slightly higher ether yields, as was the case with hexan-2-ol additions.

New Product

A GLC trace of the reaction products after several hours of reaction showed that a new product had been formed. This material had a GLC retention time less than that of hex-1-ene and was not identified. It was certainly not hex-2-ene or hex-3-ene, which might be expected from isomerisation of the hex-1-ene, since they have higher boiling points than hex-1-ene. The yield of this reaction was large with a GLC peak height of half that of the unreacted hex-1-ene value (after 7 h). It is possible that when almost all of the water has been removed from the clay by ether production and the acidity of the residual water is at a high value (*9*), isomerisation of the alkene then takes place with migration of methyl groups.

DISCUSSION

It has been found that in the sealed reaction vessels the yield of ether is lower than under reflux conditions at comparable temperatures. It is also true that under reflux some of the water initially present in the clay is displaced and held in the reflux condenser. This suggests that the ether is produced more effectively when a large number of the original water molecules have been removed, i.e., when the acidity of the interlayer region is at its greatest (*9*). Furthermore in the case of a Cu–clay equilibrated so that it contained a relatively large quantity of water (4 H_2O/cell), but which had the same basal spacing as the Cu–clay (12% rh) used elsewhere, reaction in a sealed system was very slow even at 100°C. All of the above emphasizes the crucial importance of the role of the water molecules in the reaction kinetics even within a relatively small range of clay water content.

The experimental results may be explained by the following rationalisation. The thermogravimetric evidence referred to above showed that between 1 and 2 hex-1-ene molecules per unit cell can accommodate themselves in the interlayer space. In addition the Cu–clay (12% rh) contained 3.3 water molecules per unit cell together with $\frac{1}{4}$ Cu^{2+}. If we put one of the 3.3 H_2O molecules per unit cell with the copper coordination sphere (4 H_2O per Cu), we have an average 2.3 free H_2O per unit cell. Now we can distribute this water between different unit cells so that the average remains at 2.3 H_2O/cell, but in some cells there might be 1 H_2O but a corresponding high organic content whereas in some cells there might be up to, say, 4 H_2O with little organic content. When we use a clay with 4 H_2O/cell rather than the Cu–clay (12% rh) which has 3.3 there will be a much smaller chance of finding a particular unit cell with very low water content.

We consider that hex-1-ene can be found in varying amounts in all unit cells and that hexan-2-ol is created in situations in which there is a relatively large amount of water (hex-1-ene + H_2O → hexan-2-ol). The ether, on the other hand, is preferentially formed when the local environment is relatively low in water (i.e., of high acidity (*9*)) and in a situation where hexan-2-ol and hex-1-ene coexist in close proximity (hexan-2-ol + hex-1-ene → ether).

ACKNOWLEDGMENTS

We thank the Royal Society and the Science Research Council for their support and Dr. R. Horgan and Mr. J. Heald for mass spectral data.

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Received April 14, 1981; revised November 20, 1981

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