# Chemical Conversions using Sheet Silicates: Facile Ester Synthesis by Direct Addition of Acids to Alkenes

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*Summary* Ethene and acetic acid react in the interlamellar regions of certain cation (*e.g.* $Al^{3+}$)-exchanged montmorillonites to yield ethyl acetate as the sole product, and a variety of carboxylic acids readily add to $C_2$—$C_8$ alkenes at temperatures above 100 °C to yield the corresponding esters in high and selective yields.

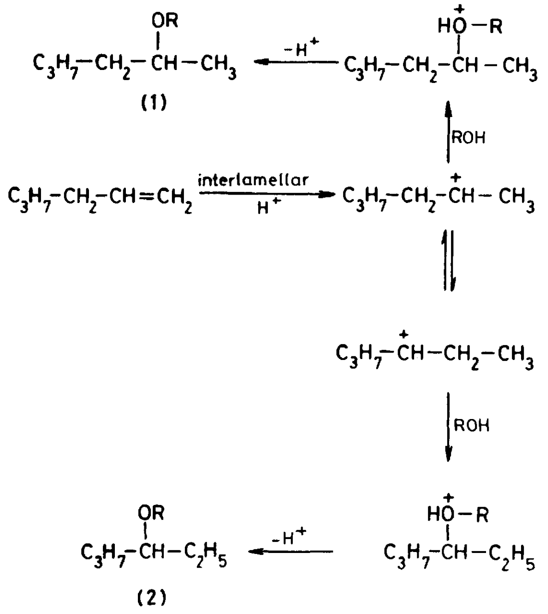
We have shown previously[1,2] that the microenvironment surrounding certain exchangeable interlamellar cations in montmorillonites is efficient in bringing about several novel organic syntheses. It was shown that the water associated with interlamellar cations (*e.g.* $Cu^{2+}$, $Fe^{3+}$, $Al^{3+}$) reacts under mild conditions with alkenes to form ethers, alk-1-enes giving the corresponding di-(alk-2-yl) ethers.

Whilst the alkene–water reaction is a stoicheiometric process, involving the coupling of intercalated water with two alkene molecules, and ceases when all the water has been consumed, the reactions involving the alcohols are genuinely catalytic since the montmorillonite may be re-used. This success has encouraged us to explore other possible reactions of OH-containing molecules, in particular the production of esters by the direct addition of carboxylic acids to alkenes. We here report the salient features of a simple, efficacious route to ester formation using readily available montmorillonite.

A variety of carboxylic acids has been shown to add readily to $C_2$—$C_8$ alkenes at temperatures above 100 °C to yield esters in very clean reactions.[3] For ethene and acetic acid, for example, the sole product is ethyl acetate with conversions beyond 90% based on acetic acid, in a 4 h reaction at 200 °C. Similarly isopropyl acetate was the sole ester product from the reaction of propene and acetic acid, comprising 83% of the product mixture. For longer-chain alkenes, however, as well as the expected Markownikoff addition products, some isomerisation occurs, thereby yielding unbranched isomeric esters. A typical product distribution for the reaction of hex-1-ene with acetic acid in the presence of the $Cr^{3+}$-exchanged montmorillonite at 200 °C is: 2-hexyl acetate, 70% and 3-hexyl acetate, 30%. The presence of so much 3-hexyl acetate establishes that isomerisation occurs readily. There is no chain branching. In the corresponding reaction with oct-1-ene, the three anticipated products resulting from acetate addition at the C-2, C-3, and C-4 positions are observed, again without chain branching.

The reactions have been mainly carried out in small stainles steel pressure vessels (*ca.* 20 $cm^3$ capacity) and a typical charge would be 1 g of solid catalyst and 5 g of reactant. The pressure vessel was immersed in a liquid thermostat capable of operating up to 220 °C. Alternatively the reactions may be carried out in a simple reflux apparatus, provided that the vapour pressures are suitable. Inert diluent solvent, *e.g.* n-alkanes, may be used to provide suitable reaction temperatures.

The reactions are associated with modest activation energies ($E$); *e.g.*, $E$ for both ethyl acetate and 2-hexyl



SCHEME.

R = alkyl: (**1**) = 1-alkyl 2-hexyl ether;
(**2**) = 1-alkyl 3-hexyl ether
R = acyl: (**1**) = 2-hexyl ester;
(**2**) = 3-hexyl ester

acetate is 30—34 kJ mol$^{-1}$ whereas for 3-hexyl acetate $E$ is 42—46 kJ mol$^{-1}$. The rates of initial reaction are thus substantial, that of hex-1-ene with acetic acid at 200 °C leading to a total acetate yield in the region of 30% over the first hour. Optimisation of product yields evidently requires consideration of both initial rate and final position of equilibrium.

All the experimental evidence to date points to the catalytic participation of interlamellar protons, a view consistent with the fact that montmorillonites and hectorites,[4] such as these, are well known to incude[1,2,5] considerable ionization of the interlamellar water. Thus, mechanistically, the reaction may be envisaged to proceed as in the Scheme (hex-1-ene used as example).

The equilibrium step is supported by the fact that 2-hexyl and 3-hexyl acetates are formed in the expected equilibrium ratio throughout the reaction.

The analogous direct addition of carboxylic acids or alcohols to isobutene catalysed by sulphuric acid is known for the preparation of t-butyl esters[6] and t-butyl ethers[7] but under these solution conditions the reactions are feasible only with alkenes that produce highly stabilised carbocation intermediates, whereas the interlamellar reactions in the sheet silicates proceed efficiently with alk-1-enes.

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