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# THE INFLUENCE OF INTERLAYER WATER ON CLAY CATALYSTS. INTERLAMELLAR CONVERSIONS OF 2-METHYLPROPENE

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Evidence is provided for two alternative pathways for the reactions undergone by 2-methylpropene between the layers of a sheet silicate catalyst ($Al^{3+}$-exchanged montmorillonite). This clay, when it initially contains *ca*. 12% interlayer water, catalyses the addition of either water or methanol to 2-methylpropene to yield, respectively, *t*-butanol or 2-methoxy-2-methyl propane (*m*ethyl *t*ertiary *b*utyl *e*ther, MTBE), whereas the same clay following deliberate dehydration acts as an effective catalyst for the oligomerisation of 2-methylpropene. Similar results are obtained with an $Al^{3+}$-exchanged synthetic hectorite.

Clay minerals are known to catalyse a variety of organic reactions.[1-4] In these reactions the clay catalysts act as Bronsted acids and the acidity is thought to arise, at least in part, from the polarization of solvent water molecules by the interlamellar cations.[1-4] In an investigation of the hydration of 2-methylpropene and the addition[5] of methanol to 2-methylpropene catalysed by $Al^{3+}$-montmorillonite, however, we have uncovered evidence to show that when the interlayer water is removed under mild conditions, the clay catalyst still shows activity but of a different kind.

When $Al^{3+}$-montmorillonite[5] or $Al^{3+}$-Laponite[6] containing the equilibrium amount of water or water and methanol are exposed to 2-methylpropene at room temperature and *ca*. 1.4 bar pressure in a batch type constant volume reactor, no visible liquid products result. Using $^{13}C$ NMR spectroscopy however, we have shown[6)] that for such clays, interlamellar reaction has actually occurred, the 2-methylpropene adding on interlayer water or methanol to yield *t*-butanol or MTBE respectively.

The above reactions, as continuous processes, were further studied in a flow system. 2-Methylpropene saturated with either water or methanol vapour was allowed to flow through a bed of clay pellets (1680 -840$\mu$m), packed in a stainless steel reactor (0.5 cm inside diameter and 6 cm in length) at a flow rate of 20 ml/min. The product stream was analysed directly by gas chromatography, using a 5.2 m stainless steel column packed with 14%, 20 M carbowax on chromosorb W. The conversions obtained are summarised in Table 1. It is noteworthy that appreciable reaction occurs at temperatures as low as 30 $^{o}$C. Also noteworthy is the fact that at higher temperatures dimerisation and oligomerisation occur concurrently, and that these processes were favoured over the above mentioned alternatives. Under the flow conditions employed here there is loss of interlayer water from the clay, particularly at higher temperatures; and the progressive increase of dimer formation with increasing temperature seems to be related to the decreasing water content of the interlamellar regions of the clay.

When the interlayer water was completely removed from the $Al^{3+}$-montmorillonite and the $Al^{3+}$-Laponite by successive washing with either methanol or ethanol, followed by drying under suction, and the resulting clay reacted with 2-methylpropene in a constant volume batch-type reactor at room temperature (*ca*. 1.4 bar pressure) a liquid product was obtained, which, analysis (gas chromatography/mass spectrometry) showed to consist of a mixture of oligomeric 2-methylpropenes. Dimers, trimers and tetramers of 2-methylpropene were identified by computer matching of their GC/MS data with those of the NBS Library of mass spectral data. The dimers 2, 4, 4-trimethylpent-2-ene and 2, 4, 4-trimethylpent-1-ene were also identified by comparing chromatographic rentention times of authentic samples.

When the interlamellar water of $Al^{3+}$-Laponite was removed by evacuation through a liquid-nitrogen trap at 300 K and the resulting clay treated with 2-methylpropene, an oligomeric mixture was again produced. However, when the $Al^{3+}$-montmorillonite was similarly dried by evacuation and treated with 2-methylpropene no liquid product was obtained, but the clay was found to have acquired a bright purple colouration. An extract of this 'complex' in methanol was again found to contain the same oligomeric 2-methylpropenes. The indications are that: (i), under similar conditions, a smaller fraction of the interlamellar water is removed from the $Al^{3+}$-montmorillonite than from the $Al^{3+}$-Laponite (see Table 2); and (ii) essentially similar processes occur in the different clays containing little or no water irrespective of the mode of water removal. (In the alcohol-treated clays small amounts of the respective tertiary butyl ethers were identified and these obviously arise from residual alcohol in the interlamellar regions).

The results from the treatment of the clays containing *ca.* 12% (w/w) water (or methanol) with 2-methylpropene at constant volume show that reactions in these cases are limited to the addition of interlayer water (or methanol) to the olefin. It is of interest to note that the resultant clay containing little or no water, but *t*-butanol or MTBE in its place, does not yield oligomeric products. On the other hand, removal of interlayer material, be it water, methanol, *t*-butanol or MTBE, prior to the 2-methylpropene treatment, leads to oligomerisation in all cases. These results may be rationalized by considering the nature of interlayer species.

As we have shown elsewhere the interlamellar $Al^{3+}$ ions undergo hydrolysis to varying degrees, to yield polymeric hydroxy-aluminium species and protons. These hydroxy-aluminium species with the associated protons are surrounded by the interlayer water molecules. Because of the strongly hydrogen bonded nature of the interlamellar water, the protons can be transmitted away from the Al-species and are thus able to protonate 2-methylpropene entering the interlamellar space. The resulting carbocations would react with interlamellar water or methanol to yield *t*-butanol and MTBE respectively. These organic products would in turn surround the proton bearing Al-species. The protons would be unable to migrate in this organic environment. Thus further protonation of unreacted 2-methylpropene leading to oligomerisation would be prevented. When the interlayer material is removed under mild dehydration however, the incoming 2-methylpropene molecules would be able to freely access the protons. The carbocations thus formed would also be able to remain attached to the Bronsted site long enough for some chain growth to proceed.

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Table 1. Conversions obtained for the flow reactions of $Al^{3+}$-montmorillonite with water and methanol. Conversions refer to normalised areas of gas chromatographic peaks

| Compound | 2-methylpropene - water reaction | | | | | | 2-methylpropene - methanol reaction | | |
|---|---|---|---|---|---|---|---|---|---|
| | 30 °C | 50 °C | 75 °C | 100 °C | 125 °C | 150 °C | 25 °C | 50 °C | 75 °C |
| 2-Methylpropene | 76.1 | 67.9 | 57.5 | 46.6 | 36.4 | 22.9 | 48.7 | 43.8 | 37.1 |
| Dimers | 0.8 | 1.4 | 10.1 | 23.2 | 36.4 | 32.2 | 7.1 | 10.7 | 24.7 |
| t-Butanol | 2.8 | 15.3 | 18.5 | 16.4 | 8.6 | 4.3 | 1.2 | 1.2 | 0.6 |
| MTBE | - | - | - | - | - | - | 25.6 | 24.6 | 18.7 |
| Oligomers | - | - | - | - | - | 20.0 | - | - | - |
| Unidentified | 17.3 | 15.3 | 10.9 | 16.4 | 8.6 | 4.3 | 14.8 | 10.8 | 8.3 |

Table 2. Conversions obtained in the oligomerisation reactions at 300 K in a batch reactor for 12 hours

| Compound | % yield (Normalized areas) | | | | | |
|---|---|---|---|---|---|---|
| | Al-Lap[a)] washed in methanol | Al-Mont$^{e}$[b)] washed in methanol | Al-Lap washed in ethanol | Al-Mont$^{e}$ washed in ethanol | Al-Lap vacuum dried | Al-Mont$^{e}$ vacuum dried |
| 2-Methylpropene | 0.02 | 14.8 | 2.0 | 3.7 | 0.09 | 0.7 |
| 2, 4, 4-Trimethyl pent-1-ene | 13.8 | 42.1 | 13.7 | 25.7 | 0.7 | 13.1 |
| 2, 4, 4-Trimethyl pent-2-ene | 4.1 | 11.2 | 4.2 | 7.0 | 0.2 | 4.7 |
| Total trimers | 54.3 | 13.6 | 46.9 | 43.6 | 29.1 | 29.6 |
| Total tetramers | 17.2 | 13.8 | 23.8 | 12.9 | 45.1 | 35.9 |
| Total unidentified oligomers | 3.7 | 0.44 | 4.8 | 2.8 | 12.8 | 15.0 |
| Others unidentified | 2.3 | 2.0 | 3.0 | 3.0 | 12.0 | - |
| 2-Methoxy-2-methyl propane | 4.1 | 1.3 | - | - | - | - |
| 2-Ethoxy-2-methyl propane | - | - | 1.3 | 0.9 | - | - |

a) Al-Lap stands for Al$^{3+}$-Laponite - see text.

b) Al-Mont$^{e}$ stands for Al$^{3+}$-montmorillonite - see text.

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8) The montmorillonite used was Gelwhite, marketed by the Georgia Kaolin Co., New Jersey.
9) Laponite is a widely used term used for a synthetic hectorite manufactured by the Laporte Company, England.

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