# Oligomerization of Dec-1-ene over Montmorillonite Clay Catalysts[†]

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The Brönsted acid sites generated on Montmorillonite-K10 and other cation ($Al^{3+}$, $Zr^{4+}$, $H^+$) exchanged clays when evacuated at high temperature are quite active for oligomerization of dec-1-ene in liquid phase.

The use of polyalphaolefins (PAOs) as high performance functional fluids is receiving acceptance in recent years.[1] Friedel–Crafts, Ziegler and free radical types of catalysts[2–4] are known to oligomerize linear alpha-olefins into low molecular mass oligomers. Apart from these catalysts heterogeneous catalysts such as $BF_3/SiO_2$, $BF_3/Al_2O_3$[5] and HKL zeolites[2] have been used for the oligomerization of alpha-olefins in the vapour phase. They offer advantages such as easy separation of the catalyst and less corrosion of the reactor. Adams *et al.* have shown that hex-1-ene and oct-1-ene in hexane solution when refluxed over cation exchanged clays[6–8] yield dialkyl ether. We have observed recently that Montmorillonite-K10 and cation exchanged clays give oligomers of dec-1-ene in liquid phase very smoothly.

Montmorillonite-K10 (Fluka, Switzerland) and dec-1-ene (E. Merck, Germany) were used without further purification. $\gamma$-$Al_2O_3$-KF (2%) was prepared by the conventional impregnation method. Montmorillonite-H, Montmorillonite-Al and Montmorillonite-Zr[9,10] were prepared by ion exchange. The surface area of the clays was measured on Carlo Erba Strumentazione using $N_2$ adsorption by the BET method. The IR spectra of pyridine adsorbed on clay were measured[11] on a Beckman 2220 spectrophotometer. Mass spectra of PAOs were recorded on a HP 5985 mass spectrometer. Maximum acidity of clays were measured by using acid–base indicators.[12]

Oligomerization of dec-1-ene was carried out by mixing 10 ml of dry dec-1-ene with the solid clay catalyst (0.5 g) for a given period of time and temperature (Table 1) under a nitrogen blanket with agitation. The catalyst samples evacuated at elevated temperature were handled under $N_2$ flow in an atmos bag (Aldrich, USA). Products were analysed on a gas chromatograph using 3% Dexsil 300 coated on 80–100 mesh chromosorb W AW column (1 m) with a temperature programming of 60–300 °C (4, 32, 50; min, °C, min). Chlorobenzene was used as internal standard. Formation of oligomers was further established by comparison with standard PAOs (Emery Chemicals, USA) and mass spectra.

Different solid acid catalysts like $\gamma$-$Al_2O_3$ (acidic), Amberlite 15, Tulison T-56 ($H^+ = 1.8$ mequiv. $ml^{-1}$) and Montmorillonite-K10 clay were examined for the oligomerization of dec-1-ene at 27 °C. Only the clay was found to be active albeit to a small extent.

The oligomerization activity of Montmorillonite clay depends on the treatment conditions (Table 1). The conversion of dec-1-ene was high when the catalyst was evacuated at 140 °C. Generally it is observed that both conversion of dec-1-ene and yield of the trimer increased with rise in evacuation temperature of the clay and reaction temperature.

Montmorillonite-H and Montmorillonite-Na exhibited the highest and the lowest oligomerization activity, respectively under these conditions. Among the various clays the activity for oligomerization of dec-1-ene followed the order: Montmorillonite-H > Montmorillonite-Zr > Montmorillonite-Al > Montmorillonite-K10 > Montmorillonite-Na. This trend corresponds to the acidity of the clay catalysts (Table 2).

The oligomerization activity of the clay materials originates from either Lewis or Brönsted acid sites available inside the interlamellar spacings or outside surface of the clay. A kinetic study of the trimerization of dec-1-ene on Montmorillonite-K10 clay shows that oligomers are not formed in the initial stages (2–4 h) and products could be detected after several hours (>10) of reaction. This is very much consistent with the reports on the interaction of substrates in the interlamellar spacings of Montmorillonite clays.[13,14] Maximum acidity of clays increase after evacuation at 140 °C for 5 h (Table 2). In the case of Montmorillonite-Al, Montmorillonite-Zr and Montmorillonite-H the acidity ($H_o$) is very high ($<-8.2$). To identify further the sites responsible for the oligomerization of dec-1-ene, pyridine adsorption studies were undertaken on the various clay catalysts. IR absorptions at 1540 and 1460 $cm^{-1}$ owing to pyridinium ion and coordinatively bonded pyridine were followed. The absorption at 1540 $cm^{-1}$ was absent in the case of Montmorillonite-Na. The same clay catalyst after evacuation at 140 °C and on pyridine adsorption

**Table 1** Oligomerization of dec-1-ene on different Montmorillonite catalysts

| Catalyst | Evacuation cond. | Reaction temp./°C | *t*/h | Conv. of dec-1-ene (%) | Product composition[a] Dimer | Trimer | Tetramer | Higher oligomer |
|---|---|---|---|---|---|---|---|---|
| 1 Montmorillonite-K10 | — | 27 | 12 | 7 | — | 50 | 50 | — |
| 2 Montmorillonite-K10 | 140 °C, 5 h | 27 | 12 | 32 | 24 | 37 | 24 | 15 |
| 3 Montmorillonite-K10 | 180 °C, 5 h | 27 | 12 | 25 | 38 | 42 | 18 | 2 |
| 4 Montmorillonite-K10 | 225 °C, 5 h | 27 | 12 | 49 | 17 | 47 | 36 | — |
| 5 Montmorillonite-K10 | 140 °C, 5 h | 70 | 6 | 76 | 25 | 48 | 22 | 5 |
| 6 Montmorillonite-K10 | 140 °C, 5 h | 140 | 6 | 81 | 51 | 30 | 19 | — |
| 7 Montmorillonite-Na | — | 25 | 12 | 12 | 21 | 55 | 23 | — |
| 8 Montmorillonite-Na | — | 50 | 5 | 9 | 18 | 53 | 29 | — |
| 9 Montmorillonite-Na | 140 °C, 5 h | 27 | 12 | 9 | 36 | 54 | 10 | — |
| 10 Montmorillonite-H | — | 27 | 12 | 9 | 82 | 18 | — | — |
| 11 Montmorillonite-H | 140 °C, 5 h | 27 | 12 | 70 | 17 | 43 | 26 | 13 |
| 12 Montmorillonite-Zr | 140 °C, 5 h | 27 | 12 | 51 | 16 | 46 | 28 | 10 |
| 13 Montmorillonite-Al | 140 °C, 5 h | 27 | 12 | 45 | 17 | 47 | 26 | 10 |

[a] Based on GC areas.

**Table 2** Surface properties of clay catalysts

| Catalyst | Max. acidity ($H_o$) | Surface area/m$^2$ g$^{-1}$ |
|---|---|---|
| Montmorillonite-K10 | +3.3 to + 1.5 | |
| Montmorillonite-K10 | −5.6 to −8.2[a] | 185.4 |
| Montmorillonite-Na | +1.5 to −3[a] | 175.9 |
| Montmorillonite-H | <−8.2[a] | 241–247 |
| Montmorillonite-Al | −8.2[a] | 174–191 |
| Montmorillonite-Zr | <−8.2[a] | 171.5 |

[a] Clays evacuated at 140 °C for 5 h.

**Table 3** Pyridine adsorption studies on Montmorillonite clays

| Clay + Pretreatment | Ratio of Brönsted : Lewis acid sites[a] |
|---|---|
| 1 Montmorillonite-K10 after adsorption of pyridine | 1:4.7 |
| 2 Montmorillonite-K10 evacuated at 140 °C + pyridine adsorbed | 1:3.2 |
| 3 Montmorillonite-H evacuated at 140 °C + pyridine adsorbed | 1:4.2 |

[a] Intensity of IR absorption at 1540 and 1450 cm$^{-1}$ divided by the mass of sample were taken for the Brönsted and Lewis acid sites, respectively.

does not show any absorption at this wavelength. This shows clearly that the concentration of Brönsted acid sites is very small on the Montmorillonite-Na catalyst and whatever activity observed could be due to acidic sites exterior to the interlamellar structure.

An IR study of Montmorillonite-K10 clay after evacuation at 140 °C followed by pyridine adsorption shows clearly that there is an increase of Brönsted acid sites (Table 3) whereas on Montmorillonite-H clay it is almost the same. On Montmorillonite-K10 and other cation exchanged clays when evacuated at elevated temperatures, not only water molecules adsorbed in the interlamellar spacings are removed but Brönsted acidic sites are created by polarisation and subsequent dissociation of water[12] molecules coordinated to metal ions. However, on Montmorillonite-H clay after evacuation at elevated temperatures, protons located on the inaccessible ion exchange sites will be shifted to the edges of sheets[15,16] for interaction with dec-1-ene.

It is pertinent to note that the composition of the oligomers remains almost the same (runs 2, 11–13) in all the clay catalysts. There appears to be an equilibrium concentration of the oligomers at 27 °C. This suggests that oligomers of dec-1-ene are formed *via* common acidic sites. An IR study of the pyridine adsorbed clay catalysts proves that the oligomerization occurs *via* a carbocation intermediate generated by the reaction of Brönsted acid sites of the clay with dec-1-ene.

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## Footnote

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