

Preliminary communication

ALUMINA SUPPORTED CpTiCl₃ CATALYTIC SYSTEM

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Summary

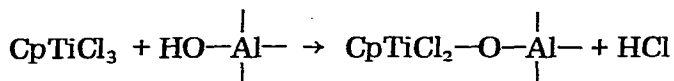
The system obtained by treating CpTiCl₃ with hydroxyl groups of alumina gel followed by reduction with BuLi was found to catalyze olefin hydrogenation at room temperature under normal pressure.

Cyclopentadienyl complexes of titanium have for some time been known as homogeneous catalysts for olefin hydrogenation [1–3]. In solid-supported catalysts, titanium is bound to the surface through cyclopentadienyl anions [3,4] or through —O—(CH₂)_n—SiMe₂—Cp groups [5].

When the metal core of the surface complex is directly bound with oxygen atoms of an inorganic support the latter has a marked effect on the activity and selectivity of the catalyst [6–8]. With regard to the above statement we have undertaken the study of catalysts containing cyclopentadienyl complexes of titanium in which the metal atom is immediately linked with oxygens of alumina.

The first step of the catalyst preparation procedure is the reaction of CpTiCl₃ with surface hydroxyl groups of the alumina carrier. The reaction is carried out in benzene solution. It proceeds with evolution of HCl.

Measurement of the amount of HCl evolved and that of unreacted CpTiCl₃ (for a known excess of CpTiCl₃) permits the determination of the quantity of CpTiCl₃ retained on the surface. When carried out for a reaction of CpTiCl₃ with alumina gel precalcined at 973K (having 0.14 mmol OH per g i.e. 0.84 OH/100 × 10⁻²⁰ m² (Å²)) these measurements provided results indicating that in this case one CpTiCl₃ combines with only one surface hydroxyl as shown below:



A similar pathway have been proposed for the reaction of CpTiCl₃ with OH group of alcohols [9] and silanols [10] in which one chlorine atom of CpTiCl₃ is replaced by an oxygen atom of the corresponding group.

Usage of alumina gel with relatively low concentration of surface hydroxyl groups prevents any possible reaction of one CpTiCl_3 molecule with two adjacent hydroxyls, the surface area covered by one CpTiCl_3 complex being relatively large, in the order of $25 \times 10^{-20} \text{ m}^2 (\text{\AA}^2)$ [4].

The yellow complex of titanium (I) formed on alumina surface gives no ESR signals; it is fairly stable to air and hydrolyzed rather slowly in water. By treating complex I with an excess of BuLi in hexane a new surface complex of titanium is obtained characterized by grey colour and a single ESR signal with $g_{\perp} = 1.9886$ and $g_{\parallel} = 1.9563$, which is typical of the Ti^{3+} ion [11]. The signal is shown in Fig. 1.

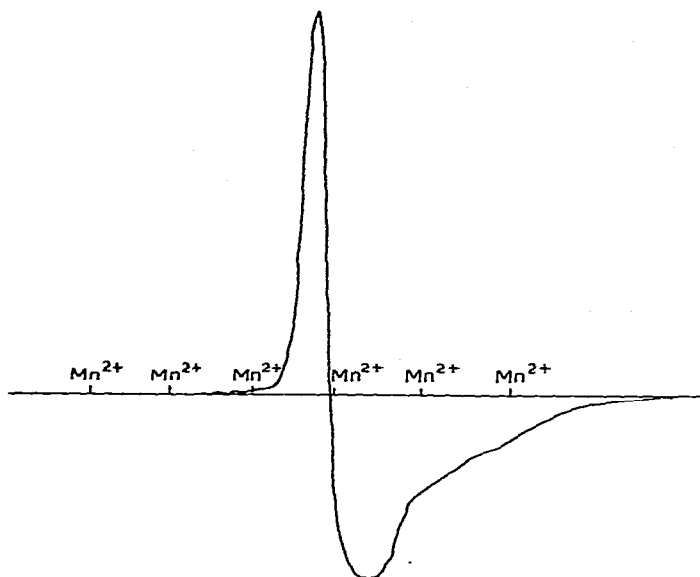


Fig. 1. ESR signal of $\text{CpTiCl}_2\text{-O-Al} + \text{BuLi}$ system recorded at room temperature (ESR standard, Mn^{2+} in MgO).

The latter complex catalyzes olefin hydrogenation under normal conditions. The results of hydrogenation experiments with ethylene, propylene, isobutylene and 1-hexene are illustrated in Fig. 2.

The catalytic tests were carried out in a static reactor of 200 ml volume. No solvent was used. The progress of the reaction was monitored by measuring the pressure drop in the reactor and by periodic GLC analyses.

Reduction of α -olefins proceeds readily at 293 K. However, any chain branching at double $\text{C}=\text{C}$ bond considerably decreases the reaction rate. Thus, e.g. very low conversion of isobutylene is observed at 293 K; only at 363 K are satisfactory results achieved. The reaction rate is effectively increased by using higher H_2 :olefin ratios.

The catalyst under consideration is inactive towards hydrogenation of butadiene and propyne-1 under normal conditions.

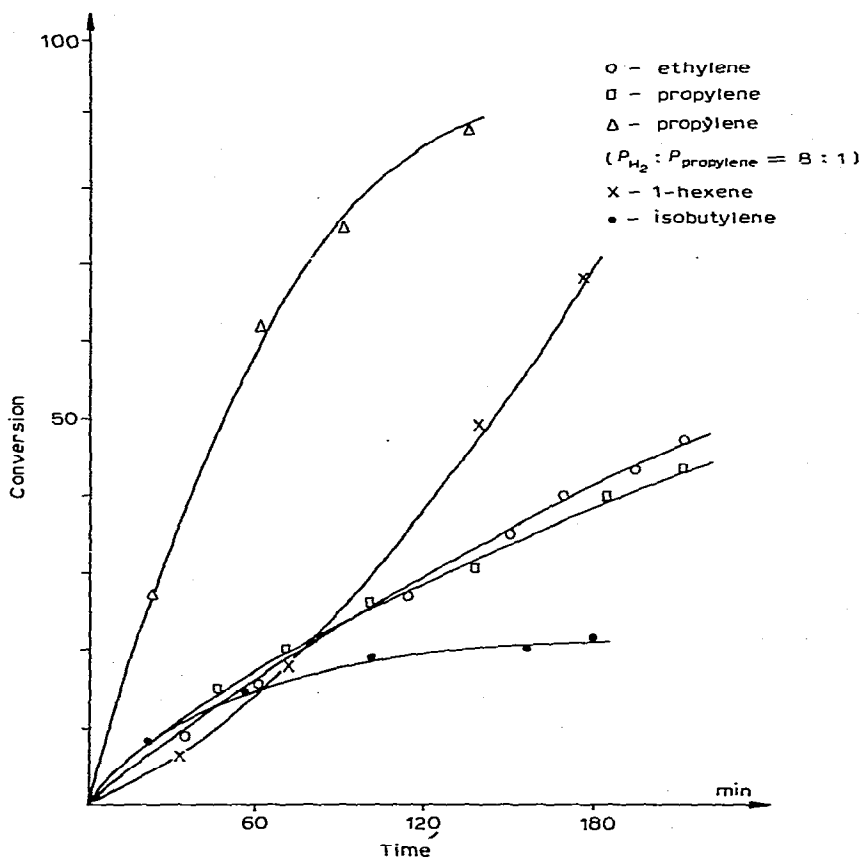


Fig. 2. Hydrogenation of olefins by alumina supported CpTiCl_3 catalytic system, 0.1 g of catalyst, 0.014 mmol Ti, reaction temperature, 293 K (363 K for isobutylene), $P_{\text{H}_2} + P_{\text{olefin}} = 1013.25$ hPa, $P_{\text{H}_2} : P_{\text{olefin}} = 4:1$.

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