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Active hydrogenation catalysts from titanium complexes and alkali metal hydrides *

Yiping Zhang, Shijian Liao *, Yun Xu,
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 100, Dalian (P.R. China)

and Shoushan Chen
Institute of Elemento-Organic Chemistry, Nankai University, Tianjin (P.R. China)

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Abstract

Hydrogenation of 1-hexene was catalyzed by titanium complexes allowed to react in situ with active alkali metal hydrides. Under normal temperature and pressure, a maximum turnover number of 2270 min^{-1} was obtained using Cp_2TiCl_2/NaH as catalyst, while a high turnover of 9290 in 80 min was achieved using a less active but more stable catalyst $[C_6H_{10}(p\text{-}CH_3OC_6H_4)C_5H_4]_2TiCl_2/NaH$. The hydrogenation rates using these catalysts have a very low temperature dependence, and are still very high even at $-30\,^\circ C$. The use of active NaH and KH as cocatalysts is the key point for the high catalyst activities.

Introduction

Titanium metallocenes have been widely studied as catalysts for the hydrogenation of unsaturated hydrocarbons [1–15]. Lithium alkyls have been commonly used as a reducing agent, although lithium aluminum hydride and its derivatives, aluminum alkyls, Grignard reagent and alkali metals have also been used. Since then, many active catalyst systems have been developed. The anchoring of titanocene species on supports has yielded even more active and more stable hydrogenation catalysts [16–21]. However to our knowledge, alkali metal hydrides have not been considered as cocatalysts for this purpose. This paper describes some results obtained on the hydrogenation of 1-hexene with binary catalysts based on various titanium complexes and active alkali metal hydrides. A feature of these catalysts is their high activity under very mild reaction conditions and even at very low temperature.

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* Dedicated to Professor Günther Wilke on the occasion of his 65th birthday.

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Results and discussion

Preliminary experiments showed that the combination of titanium complexes with commercial alkali metal hydrides which were synthesized at high temperatures [22] did not display any catalytic activity for the hydrogenation of 1-hexene. Nevertheless, hydrides synthesized by the homogeneous catalytic method at 40 °C in the laboratory fulfilled this purpose. These hydrides are different from the commercial ones by their high dispersiveness and fresh clean surface. The specific surface area measured by the BET * method was very large, 90 m^2/g for NaH and 45 m^2/g for KH. They are insoluble in toluene, actually the reaction of titanium complexes with alkali metal hydrides for the formation of catalytic active species is carried out on the solid surface. Table 1 lists some results obtained with catalyst systems based on titanium compounds using various active alkali metal hydrides as cocatalysts. Catalysts derived from $TiCl_4$ have very low but rather stable activities. $CpTiCl_3$ gives better results, while even much higher activities are obtained by Cp_2TiCl_2, using either NaH or KH as cocatalysts. For various alkali metal hydrides, LiH is only fairly active, which is probably related to its mainly covalent bond character. Both NaH and KH are effective catalyst components. Their bond characters are ionic in nature. The Cp_2TiCl_2/NaH or KH catalyst system exhibits a very high initial rate, thus the maximum turnover number may reach as high as 2270 or 1750 min^{-1}, respectively, in spite of the very poor stabilities. Their activities decay very quickly as indicated by the kinetic curves shown in Fig. 1. In the literature, the decay of the activity of titanocene catalysts was described by the dimerization of active species [16b,23,24] via abstraction of hydrogen from the cyclopentadienyl ring.

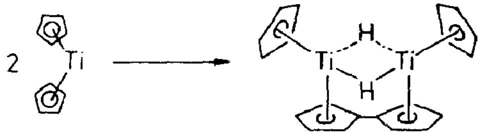

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Table 1

Hydrogenation of 1-hexene catalyzed by titanium compounds using various active alkali metal hydrides as cocatalysts
(Reaction conditions: 1 atm H_2, 10 ml toluene, 1 ml 1-hexene, cocatalyst (MH) 0.8 mmol, or 4 mmol for $TiCl_4$/MH)

Catalyst	Amount of catalyst Ti (μmol)	Temperature (°C)	Maximum turnover number [a]	Turnover [b]
$TiCl_4$/LiH	200	50	0.006	1(360)
$TiCl_4$/NaH	200	50	0.16	28(300)
$TiCl_4$/KH	200	50	0.16	28(360)
$CpTiCl_3$/KH	4	20	239	998(120)
Cp_2TiCl_2/LiH	0.8	20	184	606(30), 606(120)
Cp_2TiCl_2/NaH	0.8	20	2270	3830(120)
Cp_2TiCl_2/KH	0.8	20	1750	4170(120)

[a] Turnover number: mol H_2 uptake/mol Ti·min. [b] Turnover: mol H_2 uptake/mol Ti at the time indicated in parentheses (in min).

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* BET = Brunauer–Emmett–Teller.

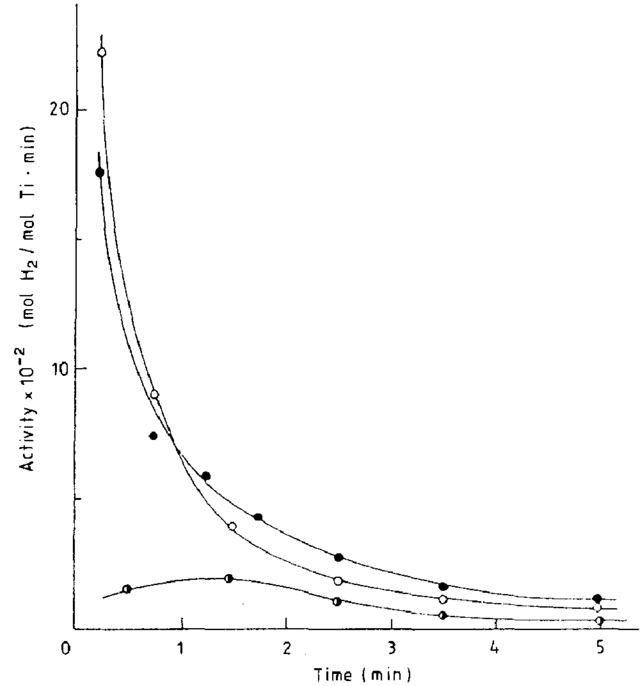
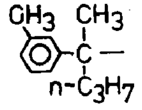


Fig. 1. Kinetic curves of 1-hexene hydrogenation catalyzed by Cp_2TiCl_2 with different cocatalysts. Reaction conditions are the same as that in Table 1. ●, Cp_2TiCl_2/KH; ○, Cp_2TiCl_2/NaH; ◑, Cp_2TiCl_2/LiH.

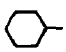
In view of that, it is possible to change the catalyst stability and activity using various substituted cyclopentadienyltitanium complexes with different steric hindrance or ease of hydrogen abstraction. The following substituted titanium complexes have been used as catalyst precursors $(RCp)_2TiCl_2$ (**1–7**), where:

(**1**) R =

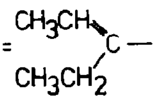


(**2**) R =

(**3**) R =

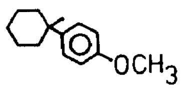


(**4**) R =

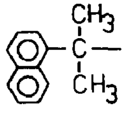


$(CH_3CH_2)_2C-$

(**5**) R =



(**6**) R =



(**7**) R=

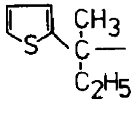


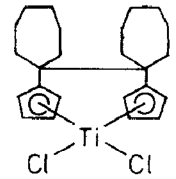
Table 2

Rates of 1-hexene hydrogenation catalyzed by various titanium complexes using NaH as cocatalyst (Reaction conditions are the same as that in Table 1)

Catalyst	Maximum rate mol H_2/mol Ti·min	Catalyst efficiency TO [a]
1/NaH	2720	3950(30) 4370(120)
2/NaH	2080	2400(5) [b]
3/NaH	1320	4090(30) 4940(120)
4/NaH	1057	2590(30) 2590(120)
5/NaH	695	7500(30) 9290(80)
6/NaH	125	1900(30) 4510(120) 6770(240)
7/NaH	92	2100(30) 4520(120) 5300(240)
8/NaH	53	325(30) 462(120)
9/NaH	438	1020(30) 1190(120)

[a] Turnover: mol H_2 uptake/mol Ti at the time indicated in parentheses (in min). [b] No activity after 5 min.

(8)



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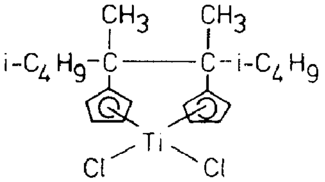
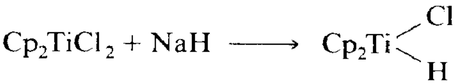


The results are shown in Table 2 and Fig. 2. From Table 2, the following tendency is observed with a few exceptions: when the steric hindrance of the substituted group on the cyclopentadienyl ring is relatively small, the titanium complex has high initial catalytic activity but poor stability (for instance, complexes **1** and **3**), whereas when the steric hindrance is large, the titanium complex has lower initial catalytic activity but better stability (for instance, complex **6**). Complex **5** has medium initial activity and fairly good stability. Its catalyst efficiency may reach a turnover of 9290 in 80 min.

In general, most of the catalyst systems which we have studied exhibit high initial rates but then lose much of their activities within a few minutes. The hydrogenation reactions then proceed at a moderate rate and are followed by a moderate rate of decay of catalyst activity. We therefore would like to suggest the possible existence of two kinds of active species. One species is formed by the reaction between titanocene dichloride (or its substituted derivatives) and NaH (or KH, LiH).



$$Cp_2TiCl_2 + NaH \longrightarrow Cp_2Ti\begin{smallmatrix}Cl\\H\end{smallmatrix} \qquad (2)$$

It has a formal oxidation state of Ti^{IV}. Active species of Ti^{IV} for the hydrogenation reactions have already been suggested in the literature [5,25]. Ti^{IV} species are very active catalytically, but they are very unstable and are easily reduced to Ti^{III} species in the presence of reducing agent. Another catalytic active species might be Ti^{III} species, which are less active catalytically but more stable. They decay slowly

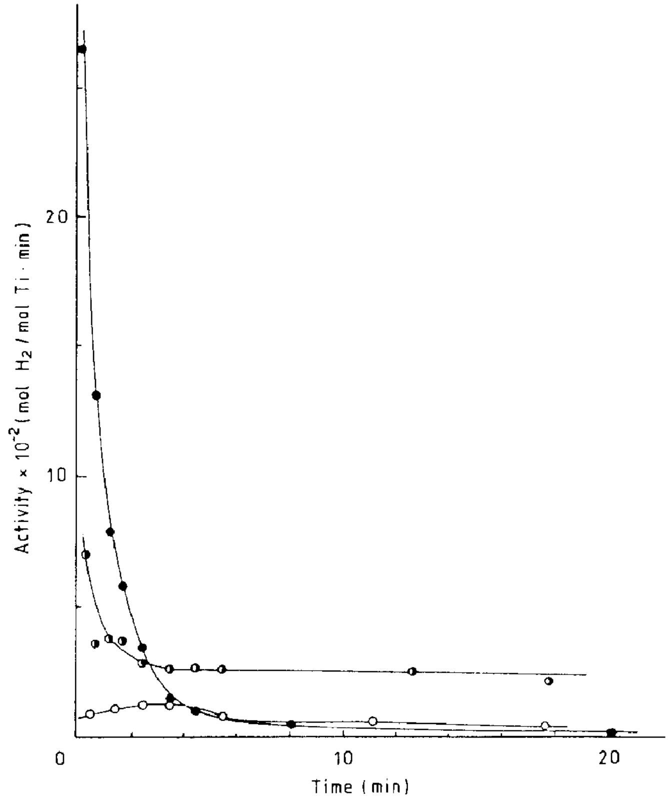


Fig. 2. Activity of the titanium complex/NaH catalyst as a function of reaction time in the hydrogenation of 1-hexene. Reaction conditions are the same as that in Table 1. ◑, **5**/NaH; ○, **6**/NaH; ●, **1**/NaH.

via a dimerization mechanism as described in eq. 1. Although the active species are formed on the surface of the insoluble alkali metal hydrides, it seems to us that the catalytic active species are soluble in toluene, hence it might be a homogeneous catalytic reaction. Of course, up to now no conclusion can be drawn without further experimental evidence.

It is noteworthy to mention that the temperature dependence of the rate of hydrogenation using these catalysts is very small. Table 3 gives an example of the

Table 3

Temperature dependence of the rate of 1-hexene hydrogenation catalyzed by Cp_2TiCl_2/KH (Reaction conditions other than temperature are the same as that in Table 1)

Temperature (°C)	Maximum rate mol H_2/mol Ti·min	Catalyst efficiency TO [a]
−30	1510	1530(30) 2040(120)
−20	1740	2370(30) 3040(120)
−10	2670	2510(30) 3000(120)
10	2810	2930(30) 3840(120)
20	1750	3400(30) 4170(120)
30	1340	1630(30) 1830(120)

[a] Turnover: mol H_2 uptake/mol Ti at the time indicated in parentheses (in min).

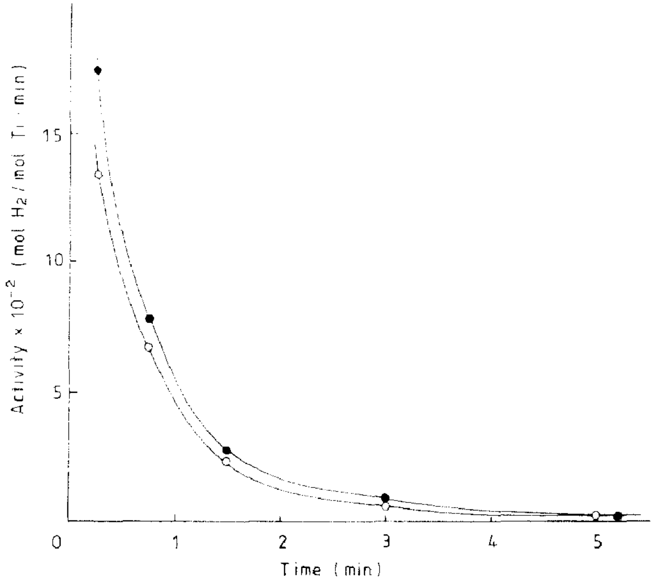


Fig. 3. Temperature effect on the catalyst activity. Reaction conditions are the same as that in Table 1 except temperature. ○, 30 °C; ●, −20 °C; Catalyst: Cp_2TiCl_2/KH.

effect of reaction temperature on the rate of hydrogenation using the Cp_2TiCl_2/KH catalyst system. The maximum rate at 20 °C is even lower than that at 10 or −10 °C, while at −30 °C the catalyst still has a maximum turnover number of 1510 min^{-1}. The reason for this small temperature dependence may be attributed to two factors: very low activation energy of the catalytic reaction and the poor thermal stability of the catalytically active species. Figure 3 shows the kinetic curves of hydrogenation carried out at 30 °C and −20 °C which indicate that the difference between the rates of decay of catalyst activity at these two temperatures is small. This implies that low activation energy is the main factor. In addition, the loss of active species is due to a fast reaction also with a low temperature dependence.

For all the catalyst systems which we have studied, no noticeable isomerization reaction took place in the hydrogenation process. The amount of 2-hexene and 3-hexene formed in the reaction mixture was negligible as indicated by GC analysis.

Experimental

In view of the high sensitivity of the catalysts to air and moisture, all manipulations were performed in an inert gas atmosphere, using Schlenk tube techniques. Argon was passed through a freshly activated Cu column at 220 °C and a 4A molecular sieve column. H_2 was purified by passing through Ni catalyst and a molecular sieve column. THF and toluene were distilled from a solution of sodium benzophenone and 1-hexene was distilled from sodium after refluxing more than 24 h under argon. Active alkali metal hydrides were prepared as follows [26]: alkali metal (100 matom, cut into ten pieces) and naphthalene (5 mmol) were placed in a dry reaction vessel already evacuated and filled with argon. It was evacuated at 10^{-2} torr for 30 min in order to remove the volatile impurities on the alkali metal surface and filled with argon again. THF (40 ml) was then added together with titanium tetrachloride (2 mmol). The argon was evacuated out and H_2 was passed into the reaction vessel under magnetic stirring until the reaction was complete. The reactions were carried out at 40 °C under normal pressure. Hydrogen uptake was measured with constant pressure gas burette. The time needed to complete the reaction for lithium, sodium and potassium is 10, 6 and 30 h, respectively. The products which were in the form of very fine grey powders were washed three times with THF (10 ml of THF each time) and then evacuated to dryness. All titanium complexes were obtained from the Institute of Elemento-Organic Chemistry, Nankai University. The reaction mixtures were analyzed by chromatography.

The hydrogenation reactions were carried out in 50 ml three necked, jacketed bottles closed with self-sealing silicon rubber caps, connected to the vacuum, argon, hydrogen lines and constant pressure gas burette. The temperature of the circulating water passing through the jacket was maintained by thermostat. Agitation was provided by means of magnetic stirring. In general, the reaction bottles were alternately evacuated and flushed with argon three times. Active metal hydride (0.8 mmol) was then added. After evacuating further three times and flushing with argon, 10 ml of toluene and 1 ml of 1-hexene were added under argon. The bottles were then evacuated and filled with hydrogen. After stirring, 1 ml of a very dilute titanium complex-toluene solution (8×10^{-4} molar solution for those very active catalysts) was injected. Hydrogen uptakes were followed by constant pressure gas burette immediately after adding the titanium complex.

In many cases, the initial turnover number was very high, the amount of catalyst used must be limited to a very low level in order to avoid the influence of the diffusion of hydrogen on the rate of hydrogenation. In our experiments, the hydrogen uptakes per minute have never exceeded 60 ml, under this condition, the rate of stirring up to a certain limit has no effect on the rate of hydrogenation as indicated by the preliminary experiments.

Acknowledgement

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