Catal Lett (2008) 124:146–149
DOI 10.1007/s10562-008-9443-3

Highly Active Catalysts for the Hydrogenation of Styrene

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Received: 1 February 2008 / Accepted: 12 February 2008 / Published online: 5 March 2008

Abstract Highly active catalysts composed of titanocene complexes and nanometric sodium hydride have been developed for the hydrogenation of styrene under normal pressure. The highest initial catalytic activity reached 138 s^{-1} (average value in the first 1 min), which is higher than previously reported data for the hydrogenation of styrene. The highest number of catalytic turnover reached 21,700 in 2 h. An effect of steric hindrance of substituents of titanocene complexes on the catalytic efficiency was observed.

Keywords Hydrogenation · Styrene · Titanocene complexes

1 Introduction

Catalysts for hydrogenation are usually composed of noble metals. Perfluoroalkylated pyridine–palladium (α) complexes catalyzed the hydrogenation of styrene in $scCO_2$ [1], TOF (initial turnover frequency) = 0.0653 s^{-1}. HRh (CO) (TPPMS)$_3$ catalyzed the hydrogenation of styrene [TPPMS = $(C_6H_5)_2P(m\text{-}C_6H_4SO_3Na)$] [2], TOF = 0.0417 s^{-1}. $[H_3Os_4(CO)_{12}]^-$ catalyzed the hydrogenation of styrene in ionic liquid [ompy][BF_4] [3], TOF = 0.163 s^{-1}. The initial catalytic activity (TOF) of the catalysts composed of nobel metals for the hydrogenation of styrene are not satisfactory. A bicomponent catalyst composed of a titanocene complex and reducing agent for the hydrogenation of olefins has attracted much attention. The reducing agents include lithium alkyls, aluminum alkyls, Grignard reagent, lithium aluminum hydride, alkali metal and alkali metal hydride [4–12]. Among them, use of nanometer-size sodium hydride as cocatalyst for titanocene complexes formed active catalysts for the hydrogenation of olefins. The initial turnover frequency (TOF) by the bicomponent catalysts composed of titanocene complexes and nanometer-size sodium hydride for the hydrogenation of styrene are 13–31 s^{-1} [12], and it was revealed only terminal alkenes can be hydrogenated by this catalyst system. But the effect of substituents of titanocene complexes on the catalytic efficiency (TO) is not clear. In this paper, we report highly active catalysts comprised of titanocene complexes with various substituents and nanometer-size sodium hydride for the hydrogenation of styrene to ethylbenzene. It provides useful information for the hydrogenation of olefins with substituents having big steric hindrance.

2 Experimental

All the substituted titanocene complexes used in the experiments were prepared in our laboratory. Nanometric sodium hydride was prepared according to the literature [13]. BET surface area of NaH is 90 m^2/g. A transmission electron micrograph shows that the average primary particle size of NaH is 23 nm.

All reaction and operations were carried out under dry argon using the Schlenk technique. Argon and hydrogen were dried and deoxygenated by a type 5A molecular sieve column and an activated Cu column at 220 °C. Toluene, styrene were dried over a type 5A molecular sieve, then

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refluxed and finally distilled from sodium and benzophenone under argon immediately before use.

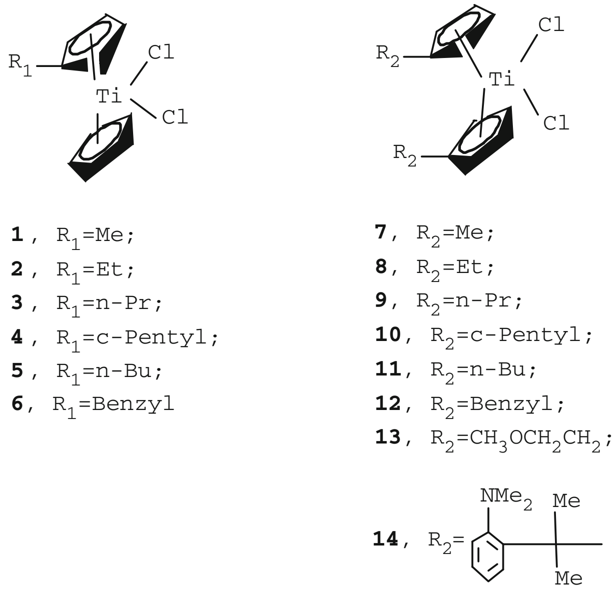
Hydrogenation of styrene was carried out in a 50 mL three-necked jacketed flask closed with a self-sealing silicon rubber septum and connected to the vacuum, argon, hydrogen lines, and to a constant-pressure gas burette. Temperature of the circulating water passing through the jacket was maintained by a thermostat. Agitation was provided by a magnetic stirrer at the rate of agitation of 1,100 r/min. The reaction flask was alternately evacuated and flushed with argon three times, and sodium hydride (20 mg) was added. After alternate evacuation and flushing with hydrogen three times further, 9 mL of toluene, 2 mL of styrene and 0.5 mL of solution of titanocene complexes in toluene (4×10^{-4} mol/L) were injected through the silicon rubber septum, and hydrogen uptakes were immediately followed by a constant-pressure gas burette. The reaction mixture was analyzed by GC in the hydrogenation.

3 Results and Discussion

In a bicomponent catalyst composed of a titanocene complex and reducing agent for the hydrogenation of olefins, it is generally believed that the breakdown in catalytic activity is due to the dimerization of active titanium species in a low valent state [4, 5], and dimerization of all active titanium species causes deactivation. Increasing the steric hindrance of substituents of titanocene complexes can slow the dimerization causing increase of catalytic efficiencies. But increasing the steric hindrance of substituents of titanocene complexes can also slow coordination of styrene and active titanium species causing decrease of catalytic efficiencies. In order to investigate relation of steric hindrance of substituents of titanocene complexes and the catalytic efficiency, a series of titanocene complexes were used in hydrogenation of styrene (Scheme 1).

Complexes **13** and **14** did not have catalytic activities, probably due to coordination of oxygen or nitrogen in complexes and titanium of active species preventing coordination of styrene and titanium of active species. Complexes **1**–**12** have excellent initial catalytic activities ($\mathrm{TOF_{initial}}$, average value in the first 1 min, 62–138 $\mathrm{s^{-1}}$) and catalytic efficiencies (TO in 2 h, 6,400–21,700), which was listed in Table 1.

The kinetic curves in Fig. 1 show that catalytic activities of **3**/NaH and **9**/NaH decrease rapidly for the first 3 min. The kinetic curves in Fig. 2 show that catalytic efficiencies of **3**/NaH and **9**/NaH increase slowly after rapid increase for the first 3 min, which is consistent with the rapid decrease of catalytic activities of **3**/NaH and **9**/NaH for the first 3 min. However, catalytic activities can exist in 2 h.



Scheme 1

Table 1 Results of the hydrogenation of styrene[a]

Catalyst	$\mathrm{TOF_{initial}}$ [mol/(mol s)]	TO (mol/mol) (in 2 h)
1/NaH	72	6,400
2/NaH	62	9,500
3/NaH	102	13,700
4/NaH	112	15,500
5/NaH	122	18,500
6/NaH	113	21,700
7/NaH	107	9,400
8/NaH	108	9,700
9/NaH	90	16,000
10/NaH	75	13,300
11/NaH	138	11,000
12/NaH	120	8,900

[a] Reaction condition: 1.01325×10^5 Pa, 303 K, 0.2 μmol Ti, 20 mg NaH, 2 mL styrene, 9 mL toluene, 2 h

The effect of steric hindrance of substituents of titanocene complexes employed on the catalytic efficiency is clear (Fig. 3). In mono(substituted cyclopentadienyl) titanocene complexes (**1, 2, 3, 4, 5, 6**), catalytic efficiencies (TO in 2 h) increase with increase of steric hindrance of substituents of titanocene complexes. In bis(substituented cyclopentadienyl) titanocene complexes, catalytic efficiencies (TO in 2 h) firstly increase and then decrease with increase of steric hindrance of substituents of titanocene complexes (**7, 8, 9, 10, 11, 12**). This is probably due to two roles of bigger steric hindrance of substituents of titanocene complexes on catalytic efficiencies: one is that bigger steric hindrance of substituents of titanocene complexes

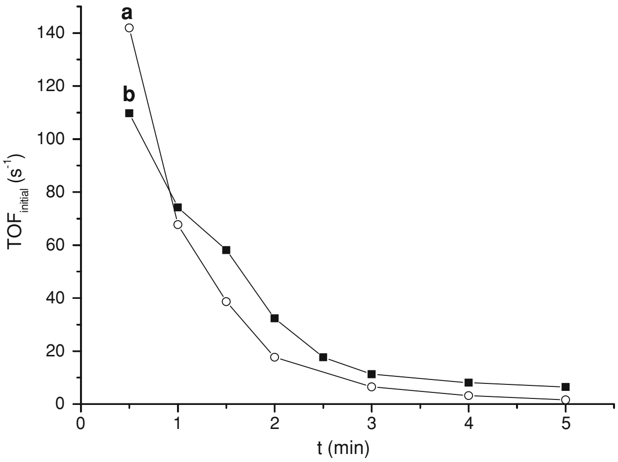


Fig. 1 Catalytic activities-time curves. (**a**) **3**/NaH; (**b**) **9**/NaH

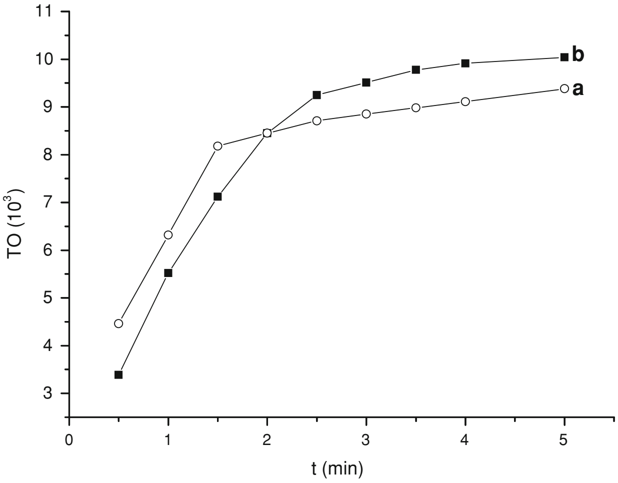


Fig. 2 Catalytic efficiencies–time curves. (**a**) **3**/NaH; (**b**) **9**/NaH

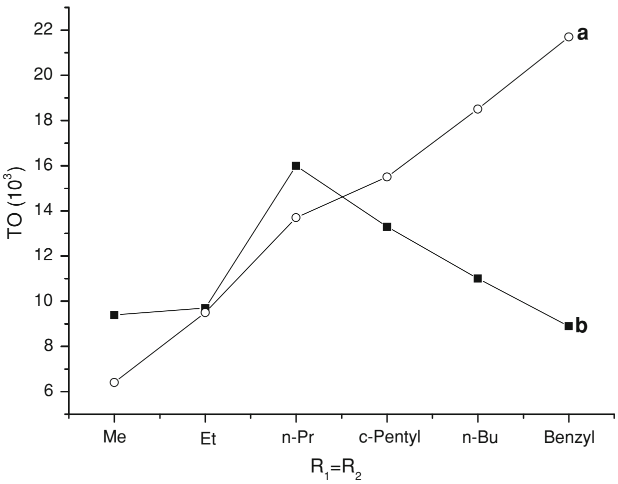


Fig. 3 Comparison of catalytic efficiencies of titanocene complexes employed. (**a**) Mono(substituted cyclopentadienyl) titanocene complexes; (**b**) Bis(substituted cyclopentadienyl) titanocene complexes

Table 2 Effects of temperature on catalytic reaction for titanocene complex **3**[a]

T (K)	$1/T$ (10^{-3} K^{-1})	TOF $_{initial}$ (s^{-1})	lnTOF	TO (in 2 h)
315	3.17	164	5.10	14,000
303	3.30	146	4.98	13,700
284	3.52	114	4.74	10,800
275	3.64	100	4.61	7,900
256.5	3.90	55	4.01	3,600

[a] Reaction condition: 1.01325 × 10^5 Pa, 0.2 μmol Ti, 20 mg NaH, 2 mL styrene, 9 mL toluene, 2 h

can slow dimerization of active titanium species causing increase of catalytic efficiencies, another is that bigger steric hindrance of substituents of titanocene complexes can slow coordination of styrene and active titanium species causing decrease of catalytic efficiencies.

The effect of hydrogenation temperature on $TOF_{initial}$ for complex **3**/NaH was investigated. The results are listed in Table 2. A plot of lnTOF versus 1/*T* (Fig. 4) was made using data in Table 2, the points representing 315, 303, 284 and 275 K are linear, and the point representing 256.5 K is down to the line. It indicates that active titanium species comprise of many components including Ti(II), Ti(III) and Ti(IV) species; when hydrogenation temperature is 315, 303, 284 and 275 K, the active titanium species was the same one; when hydrogenation temperature is 256.5 K, the active titanium species was not as the same as that in 315, 303, 284 and 275 K causing increase of activation energy of hydrogenation. The activation energy of hydrogenation at 275–315 K for complex **3**/NaH can be calculated from the slope of the line as 20.3 KJ/mol according to Arrhenius equation. The activation energy of hydrogenation of styrene by perfluoroalkylated pyridine–palladium

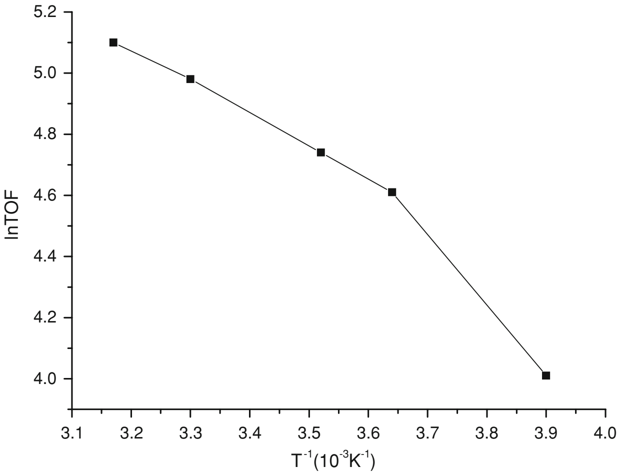


Fig. 4 TOF(s^{-1})-temperature curve for **3**/NaH in hydrogenation of styrene

(α) complexes in $scCO_2$ was 25.5 KJ/mol [1]. The activation energy of hydrogenation of styrene in this paper is lower than that in literature [1].

In conclusion, highly active catalysts composed of titanocene complexes and nanometric sodium hydride were reported for the hydrogenation of styrene. The highest initial catalytic activity ($TOF_{initial}$) reached 138 s^{-1}, which is higher than previously reported data for the hydrogenation of styrene. The highest catalytic efficiency (TO) reached 21,700 in 2 h. The effect of steric hindrance of substituents of titanocene complexes employed on the catalytic efficiency was observed.

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