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Influence of ligands and cocatalyst on the activity in ethylene polymerization of soluble titanium complexes

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Abstract

Known and new titanium complexes bearing alkoxy, phenoxy, carboxylate and cyclopentadienyl ligands in addition to chlorine have been tested towards ethylene polymerization after activation with aluminum alkyls (AlR_3) or methylalumoxane (MAO). In the absence of cyclopentadienyl ligands the optimal productivity obtained is very similar either with AlR_3 or MAO, but higher MAO/Ti than AlR_3/Ti ratios are necessary. In the case of complexes with the Cp ligand much better productivity can be obtained with high MAO ratios thus confirming that under these conditions a different activation mechanism is operative.

Key words: titanium; ethylene; polymerization; aluminum; trialkyl; methylalumoxane

1. Introduction

At present, many high activity catalysts for ethylene polymerization are obtained by coprecipitation of titanium and magnesium chloride species by chlorination of soluble compounds of these metals [1,2]. Even if most of the original organic ligands are removed by chlorine exchange, a significant amount remains incorporated in the solid catalyst; in any case systems with distinct behaviour can be formed depending on the ligands around the transition metal in the original compounds.

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The presence of organic ligands attached to Ti atoms in the active sites may affect the catalytic process also in connection with the aluminum compound used as cocatalyst.

In an effort to clarify the above points the present paper reports comparative data on the catalytic activity displayed during ethylene polymerization by soluble titanium complexes with oxygenated and/or cyclopentadienyl ligands activated with aluminum alkyls or alumoxane. The results are discussed with reference to the combination of titanium complex versus cocatalyst necessary to obtain the highest catalytic activity. On the other side the testing of these systems in solution provided opportunity of evaluating the role of ligands in determining activation by specific cocatalysts. Thus comparative experiments were performed with trialkylaluminum or methylalumoxane (MAO) to put more light on the understanding of the mechanism of action of the metallocene based catalysts [3–6] versus the more traditional systems [1].

2. Experimental

2.1. General considerations

All manipulations of moisture sensitive compounds were performed by using standard vacuum and Schlenk line techniques. All solvents were dried by distillation on sodium/potassium–benzophenone ketyl under argon atmosphere. Trimethylaluminum (Aldrich), diethylaluminum chloride, triethylaluminum, triisobutylaluminum and MAO (4.5 M in toluene) (Witco), titanium(IV) chloride and titanium alkoxides (Aldrich) were used as received. All ^{1}H NMR spectra were obtained by using Varian GEMINI 200 spectrometer.

2.2. Preparation of dichloro[pyrocatecholate]titanium(IV) ($PcTiCl_2$)

A solution of 40 mmol (4.4 g) of the pyrocatechol in 80 ml of dry toluene was added dropwise to a stirred solution of 40 mmol of $TiCl_4$ (7.6 g) in 35 ml of the same solvent at −10°C; HCl was evolved. The resulting solution was warmed to room temperature, then refluxed for a further 4 h until gas evolution ceased; the solution was cooled to room temperature and formation of black crystals was observed [7–9]. The product was filtered, washed with toluene/hexane and vacuum dried (0.01 mmHg) for several hours to provide 7.5 g of $PcTiCl_2$ (84% yield). Found: C, 31.4; H, 1.71; Cl, 31.43. Calcd.: C, 31.77; H, 1.76; Cl, 31.25. ^{1}H NMR(CD_3OD): δ (ppm) 6.8 (s, br).

2.3. Preparation of bisnonanoate dichlorotitanium(IV) (N_2TiCl_2)

A solution of 60 mmol (9.48 g) of nonanoic acid in dry n-heptane was added dropwise to a stirred solution of 30 mmol (5.71 g) of $TiCl_4$ in 25 ml of the same solvent at −25°C; HCl was evolved. The resulting solution was warmed to room temperature then refluxed for a further 6 h until the evolution of HCl ceased. The solution was cooled to room temperature and the product crystallized from n-heptane/pentane, 1:2, was vacuum dried. Green crystals were collected to provide 10 g of the product (78% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.9 (t, 3H), 1.3 (s, br, 10H), 1.65 (m, br, 2H), 2.39 (t, 2H).

2.4. *Preparation of cyclopentadienylpyrocatecholate chlorotitanium(IV) (CpPcTiCl)*

A solution of 40 mmol (2.88 g) of cyclopentadienyl lithium in toluene was added dropwise to a stirred slurry of 38 mmol (8.5 g) of $PcTiCl_2$ in 30 ml of the same solvent at 0°C. The solution was warmed to room temperature then mechanically stirred for 2 days; the product was filtered and crystallized twice from toluene/n-heptane 1 : 1; brown crystals were collected (5 g, 50% yield). Found: C, 50.4; H, 3.1; Cl, 14.2. Calcd.: C, 51.4; H, 3.5; Cl, 13.8. ^{1}H NMR ($CDCl_3$) δ (ppm): 6.5 (s, 5H), 7.1 (s, br, 4H).

2.5. *Preparation of pentamethylcyclopentadienyltrimethylsilane (Cp*SiMe$_3$)*

36.6 mmol (1.43 g) of potassium were added at 0°C to a solution of 5 g (37 mmol) of pentamethylcyclopentadiene in 200 ml of dry THF. The solution was warmed to room temperature and refluxed for 8 h. The resulting white suspension was cooled at 0°C and 34 mmol (4.4 ml, 3.7 g) of Me_3SiCl (distilled under argon and dried on molecular sieves) were added dropwise. The resulting mixture was warmed at room temperature and stirred for 12 h, then filtered to give a clear slightly yellow solution. THF was evaporated under moderate vacuum to leave pure Cp^*SiMe_3 [10] (7 g, 77% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): -0.15 (s, 9H), 1.8 (s, 15H).

2.6. *Preparation of pentamethylcyclopentadienyl trichlorotitanium(IV) (Cp*TiCl$_3$)*

A solution of Cp^*SiMe_3 (26 mmol, 7 g) in 50 ml of toluene was added dropwise to 5 g (26 mmol) of $TiCl_4$ in 200 ml of the same solvent. The red solution was stirred further for 10 h and the solvent evaporated under vacuum to leave red crystals of the title compound [10] (6.8 g, 90% yield). Found: C, 40.8; H, 4.9; Calcd.: C, 41.5; H, 5.3. ^{1}H NMR($CDCl_3$): δ (ppm): 2.3 (s).

3. Results

3.1. *Catalytic complexes*

In order to reproduce as closely as possible the situation of the active sites in $MgCl_2$ supported catalyst and possibly have a comparable activation mechanism both with AlR_3 or MAO, all of the investigated Ti complexes contained organic ligands and chlorine. These complexes were prepared as described in Section 2 according to the general simple routes reported in the literature.

According to what is generally known about the reactivity of Ti–Cl species towards aluminum alkyls, one could predict that the following reaction occurred when one of the complexes was mixed with AlR_3 [11]:

$$\geqslant\!\mathrm{Ti}-\mathrm{Cl}+\mathrm{AlR_3}\ (\text{or }\mathrm{AlR_2Cl}) \rightarrow\ \geqslant\!\mathrm{Ti}-\mathrm{R}+\mathrm{AlR_2Cl}\ (\text{or }\mathrm{AlRCl_2})$$

As we are working with Al/Ti ratios greater than one, this reaction could proceed further, particularly when two chlorine atoms are present in the starting Ti complex [12]. In this case Ti^{III} and even Ti^{II} species could be formed by disproportionation [13]. However in all experiments described here, the Al/Ti ratio was such to avoid formation of solid products during catalyst activation and ageing.

When alumoxane was used as cocatalyst it is reasonable that the reaction occurring is similar to that for Cp_2TiCl_2, apart from the obvious different stability of activated (cationic) species with different ligands.

3.2. Polymerization of ethylene

Polymerization experiments were carried out under inert atmosphere by adding the selected amount of cocatalyst to a solution of the Ti complex in toluene, cyclohexane or heptane. After the indicated ageing time, ethylene was introduced and its partial pressure kept at 1 bar during the entire polymerization, and the slurry was stirred mechanically while thermostated at the reported temperature. Tables 1–4 contain the results obtained with the various Ti complexes and $AlEt_3$, $AlEt_2Cl$, $Al(i\text{-}Bu)_3$ and MAO as respective cocatalysts. Productivity (average polymerization rate) during the first 60 min of polymerization, was reported as SA, in kg PE/Ti g atom•h•bar, and SA*, in kg PE/g atom Ti•g atom Al•h•bar.

SA and SA* appear to be affected by the ligands in the starting Ti complex, the Al/Ti molar ratio and the type of aluminum compound; variations are not dramatic and remain within one order of magnitude. Moreover, in all cases an optimal Al/Ti ratio seems to exist.

In particular with bisnonanoate titanium dichloride, MAO appears to give a 2–3 times larger SA than $AlEt_3$, but the Al/Ti ratio has to be 20–30 times higher and SA* is then markedly lower (Table 1). With dichloro(pyrocatecholate) titanium SA is very little affected by cocatalyst and Al/Ti ratio, but SA* is again appreciably larger with aluminum alkyls than with MAO (Table 2).

Cyclopentadienylpyrocatecholate monochlorotitanium shows very low activity with aluminum alkyls, whereas MAO gives one order of magnitude increase; SA* is in this case comparable for the two cocatalysts (Table 3). Mono(pentamethylcyclopentadienyl) tita-

Table 1
Polymerization of ethylene by bisnonanoate dichlorotitanium(IV)[a]

Cocatalyst	[Al]/[Ti]	SA[b]	SA*[c]
$AlEt_3$	3.0	3.7	1.20
	4.0	5.8	1.50
	4.5	5.6	1.20
	5.0	4.1	0.80
MAO	100	16.7	0.20
	200	14.3	0.07
	300	12.7	0.04
	500	8.7	0.02

[a] In n-heptane, $P_{ethylene} = 1$ bar, $T = 25°C$.
[b] In kg PE/g atom-Ti•h bar.
[c] In kg PE/g atom Ti•g atom Al•h bar.

Table 2
Polymerization of ethylene by dichloro[pyrocatecholate]titanium(IV)[a]

Cocatalyst	[Al]/[Ti]	T (°C)	SA[b]	SA*[c]
Al(iBu)$_3$	7.0	25	1.9	0.27
AlEt$_3$	1.5	0	5.7	3.80
		25	4.7	3.13
		40	3.0	2.00
		50	0.6	0.40
AlEt$_2$Cl	4.0	40	5.3	1.33
MAO	100	25	7.2	0.072
	300	25	6.0	0.020
	500	25	2.9	0.005

[a] In toluene, $P_{\text{ethylene}} = 1$ bar, $T = 25$°C.
[b] In kg PE/g atom Ti·h bar.
[c] In kg PE/g atom Ti·g atom Al·h bar.

Table 3
Polymerization of ethylene by cyclopentadienyl pyrocatecholate monochlorotitanium(IV)[a]

Cocatalyst	[Al]/[Ti]	SA[b]	SA*[c]
AlEt$_3$	4	0.15	0.03
	9	0.40	0.04
	11	–	–
AlEt$_2$Cl	2	–	–
	4	2.10	0.52
	6	0.17	0.12
MAO	100	33.40	0.33
	200	16.20	0.08
	300	15.70	0.05

[a] In toluene, $P_{\text{ethylene}} = 1$ bar, $T = 25$°C.
[b] In kg PE/g atom Ti·h bar.
[c] In kg PE/g atom Ti·g atom Al·h bar.

nium trichloride appears to be more active with AlR$_3$ than MAO, SA being 4–7 times and SA* up to 100 times larger (Table 4).

The kinetic profiles for adequately aged, catalytic systems (ageing for more than 10 min) are similar and correspond to the well known decay profile, the polymerization rate (R_p) decreasing rapidly in the first few minutes after ethylene addition and reaching a substantially constant value after 40–60 min (as shown for N$_2$TiCl$_2$ activated either with AlEt$_3$ or MAO) (Fig. 1). It is of interest to note that at least in the case of N$_2$TiCl$_2$ at 25°C, the R_p with MAO is about 4.5 times that with AlEt$_3$ after 15 min and decreases to 3.0 times after 60

Table 4
Polymerization of ethylene by monopentamethylcyclopentadienyltitanium(IV) trichloride[a]

Cocatalyst	[Al]/[Ti]	Solvent	SA[b]	SA*[c]
$AlEt_3$	4	n-heptane	4.0	1.000
	6	n-heptane	6.2	1.030
	8	toluene	7.2	0.900
	9	toluene	4.8	0.540
	11	n-heptane	5.1	0.510
MAO	100	toluene	0.8	0.008
	200	toluene	1.1	0.005
	400	toluene	0.7	0.002

[a] $P_{ethylene}$ = 1 bar, T = 25°C.
[b] In kg PE/g atom Ti·h bar.
[c] In kg PE/g atom Ti·g atom Al·h bar.

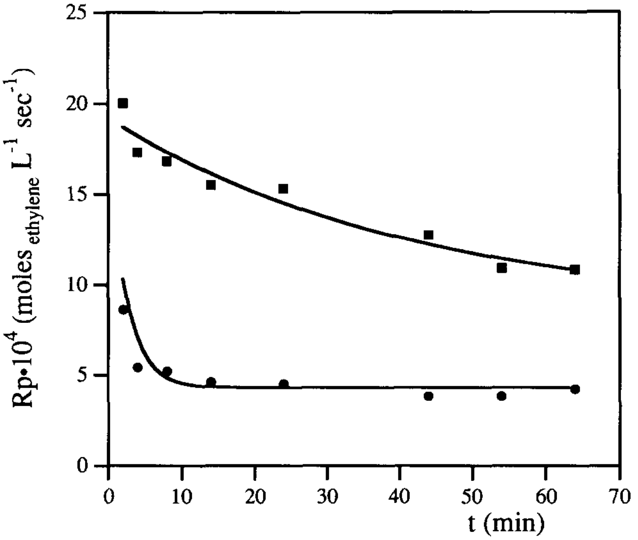

Fig. 1. Time dependence of ethylene polymerization rate for bisnonanoate dichlorotitanium(IV) (N_2TiCl_2) activated respectively with (●) $AlEt_3$ and (■) MAO in n-heptane at 25°C, molar ratio Al/Ti = 4 and 180, respectively.

min. The complexes with two Cl attached to Ti (N_2TiCl_2 and $PcTiCl_2$) show very similar decreases of SA versus time (Table 5).

The time decay of R_p in the case of Cp^*TiCl_3 is very fast with $AlMe_3$, probably due to reduction of Ti (Fig. 2).

At a lower temperature (0°C) the kinetic profile in the presence of the $N_2TiCl_2/AlEt_3$ system shows an activation period and R_p reaches a maximum value after about 30 min; after 60 min the rate is more or less the same as at 0°C (Fig. 3).

Table 5
Time dependence of SA[a] of the catalytic system (**A**) $PcTiCl_2/MAO$ and (**B**) N_2TiCl_2/MAO[b]

T (min)	**A**[c]	**B**[d]
15	12.5	14.3
30	10.8	11.7
45	8.3	10.2
60	7.2	9.1

[a] In kg PE/g atom Ti·h bar.
[b] $P_{ethylene}$ = 1 bar, T = 25°C.
[c] Al/Ti = 100.
[d] Al/Ti = 180.

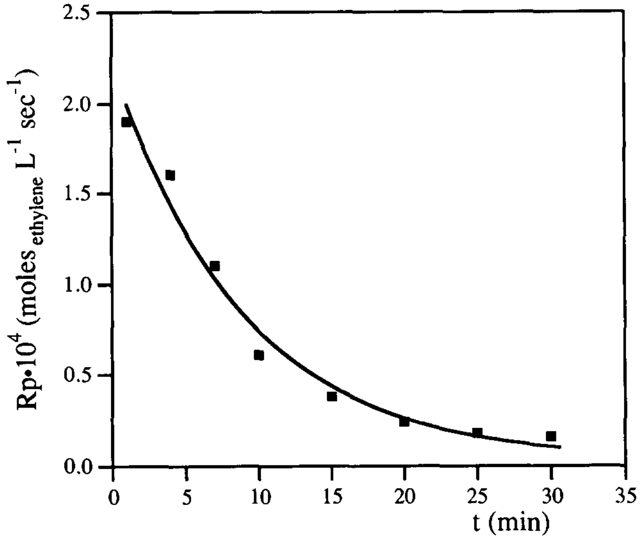

Fig. 2. Time dependence of ethylene polymerization rate for pentamethylcyclopentadienyltrichlorotitanium(IV) (Cp^*TiCl_3) activated with $AlMe_3$ in toluene at 25°C, molar ratio Al/Ti = 6.

3.3. Structure of polyethylene

The polyethylene obtained in the different polymerization experiments was characterized by FT-IR, DSC, and viscosity measurements.

The polyethylenes prepared show intrinsic viscosity in Decalin at 135°C greater than 0.8 dl/g (0.08 l/g) corresponding to $\bar{M}_v$ of more than 40000. GPC was possible only with the sample prepared in the presence of PcCpTiCl/MAO 1/100 ($\bar{M}_w = 121000$, $\bar{M}_w/\bar{M}_n = 3.64$) as the remaining samples were not soluble under the adopted experimental conditions. In all cases FT-IR spectra correspond to linear polyethylene, and are very similar; as a typical example the spectrum of the polymer prepared by $N_2TiCl_2/AlEt_3$ catalyst is shown in Fig. 4.

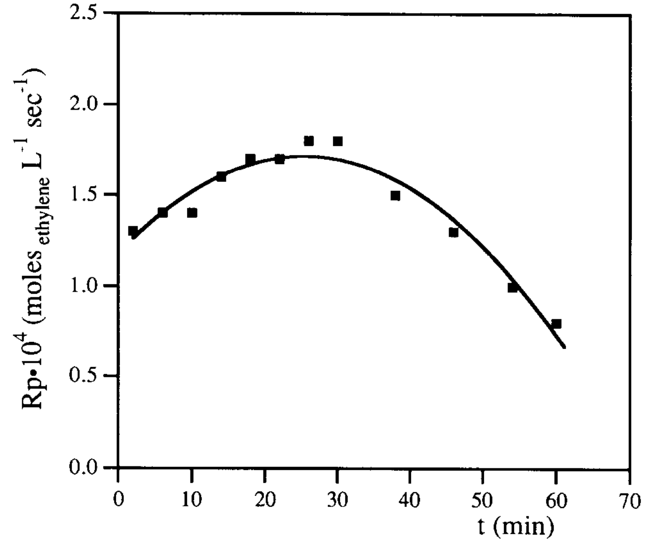

Fig. 3. Time dependence of ethylene polymerization rate for bisnonanoate dichlorotitanium(IV) (N_2TiCl_2) activated with $AlEt_3$, in n-heptane at 0°C, molar ratio Al/Ti = 4.

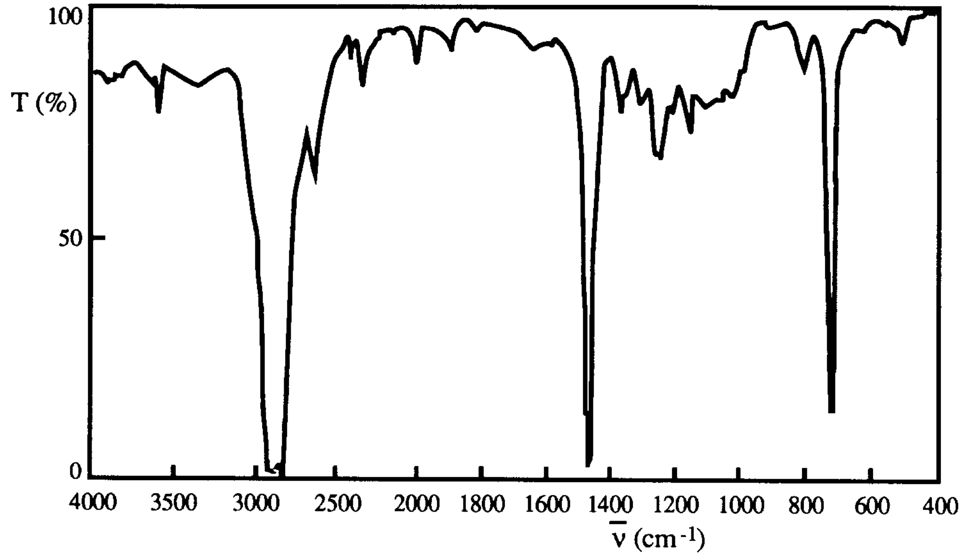

Fig. 4. FT-IR spectrum of polyethylene prepared in the presence of bisnonanoate dichlorotitanium(IV) (N_2TiCl_2) activated with $AlEt_3$.

Also DSC traces are similar for polymers prepared in the presence of different catalysts and correspond to highly linear polyethylene with melting point (onset) in the range 391–401 K and 60–70% crystallinity.

4. Discussion

A first insight into the behaviour of different catalytic systems used in the present work is obtained by comparing the best productivity (SA and SA*) obtained in various cases and relevant Al/Ti ratio (Table 6). Also as a reference, data concerning titanium tetrabutanolate [$Ti(n\text{-}OBu)_4$], and 2-ethylhexanolate [$Ti(2\text{-}EH)_4$] and Cp_2TiCl_2 are reported. Cl-containing complexes are more active under any conditions. Moreover, when Cp is not present, $AlEt_3$ and MAO give SA of the same order of magnitude, but higher Al/Ti ratios are necessary for the latter. In any case the Al/Ti ratios for the best activity are much lower than for Cp_2MeX_2 which however provides much larger activity per Ti atom (SA) suggesting a better activation than for complexes not containing Cp ligands. Even if the presence of Cp ligand [14,15] substantially activates the complex versus MAO, SA* remains lower than that with $AlEt_3$.

Cp^*TiCl_3 shows unusual behaviour and is always more active with $AlMe_3$ rather than MAO. This is substantially in agreement with an excessive Ti reduction with the massive MAO necessary.

The characterization of the catalytic systems and their kinetic behaviour as well as polymer features suggest that the polymerization mechanism is substantially the same for all transition metal complexes examined in the presence of either aluminum alkyls or alumoxane. The formation of active species should consist of alkylation of titanium by replacement of chlorine atoms with alkyl groups and consequent formation of unsaturated active species [1,13]. When Cp ligands are not present, AlR_3 and MAO show more or less the same productivity, and a lower amount of the former is required. Such behaviour can be tentatively interpreted by considering that AlR_3 is the actual cocatalyst and therefore an

Table 6

Polymerization of ethylene by various titanium(IV) complexes activated with different aluminum derivatives[a]

Catalyst	Cocatalyst	[Al]/[Ti]	SA[b]	SA*[c]
$Ti(n\text{-}OBu)_4$	$AlEt_2Cl$	6	0.08	0.013
	MAO	200	0.70	0.004
$Ti(2\text{-}EH)_4$	$AlEt_2Cl$	5	0.90	0.180
	MAO	30	0.80	0.027
$PcTiCl_2$	$AlEt_3$	1.5	5.70	3.800
	MAO	100	7.20	0.072
$CpPcTiCl_2$	$AlEt_3$	9	0.40	0.040
	MAO	100	33.40	0.330
N_2TiCl_2	$AlEt_3$	4	5.80	1.450
	MAO	100	16.70	0.167
$CpTiCl_3$	$AlMe_3$	8	7.20	0.900
	MAO	200	1.10	0.005
Cp_2TiCl_2	$AlEt_2Cl$	2.5	3.70	1.480
	MAO	3000	300	0.100

[a] $P_{ethylene} = 1$ bar, $T = 25°C$.

[b] In kg PE/g atom Ti·h bar.

[c] In kg PE/g atom T·ig atom Al·h bar.

appropriate amount of MAO is necessary to attain the optimal AlR_3/Ti ratio. When the Cp ligand is present [16], MAO becomes more effective in giving high productivity at rather high MAO/Ti ratios, thus suggesting that, at least at that concentration level, a different activation mechanism can be operative.

The different polymerization rates and activities observed when changing catalyst can arise from different propagation rate constants (k_p) and/or active sites concentration ([C*]) [17] according to the generally accepted equation

$$R_p = k_p[C^*][M]$$

which seems to hold for both catalysts, Cp containing and Cp absent [18,19].

These differences are the result of the effect of the ligands on the reaction between the titanium complexes and cocatalyst, which determines [C*] and the steric and electronic effects on the Ti–C bond, which in turn determine the k_p value. In the case of MAO, stabilization and activation of cationic species is probably also effective [18].

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