Proton NMR Studies of Supported Titanium Catalyst for Quantification of Incorporated Internal Electron Donor

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Abstract

Proton NMR method developed for quantification of internal donor incorporated in supported titanium catalyst. 1,1,2,2-tetrachloroethane was used as internal standard for quantification. The calibration curve was prepared and found linear for the desired range. This method was demonstrated for quantification of diisobutyl phthalate in catalyst. Method was resulted in good quantitative estimation of organic species in catalyst, which makes FT-NMR as an alternate analytical tools for quantitative and qualitative analysis.

Keywords:

FT-NMR, Diisobutyl phthalate, supported titanium catalyst

1. Introduction

High performance supported titanium catalyst consist of magnesium dichloride containing titanium tetrachloride and electron donor. Various internal donors such as organic monoester, diester and diether compounds are incorporated as internal donor components [1-4]. The concentration and nature of donor found to influence the stereospecificity as well as productivity of the catalyst for the propylene polymerization [4]. Chromatographic techniques such as gas chromatography and high performance liquid chromatography [5-7] are used as identification and quantitative estimation of organic compounds. NMR spectrometry is known for identification of organic compounds. It is also well suited for quantification because the signal intensity is directly proportional to the amount of nuclei [8-10].

Our interest in development of high performance supported titanium catalyst for polyolefin [1, 11-13] is focused not only on development of catalyst but also analytical methodology for qualitative and quantitative estimation. In view of this, we initiated the study on employing NMR approach to develop method for analyzing organic donor. The current paper presents our data on estimation of diisobutyl phthalate in supported titanium catalyst using NMR spectroscopy.

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2. Experimental

2.1. Materials and Methods

2.1.1. Chemicals

NMR solvent methanol-d4 was used for sample preparation and of NMR grade with 99.8% deutration with 0.03% tetramethyl silane as internal standard and purchased from Sigma-Aldrich. 1,1,2,2- Tetrachloroethane (TCE) was used as internal standard for quantification and of analytical reagent grade from Labort Chemicals, India. Diisobutyl phthalate (DIBP) was used as standard for calibration and procured from Labort Chemicals, India. All the solutions were freshly prepared.

2.1.2. Instrument

The proton NMR spectrum was measured with a Bruker FT NMR Avance 400 spectrometer at 400 MHz, using tetramethyl silane as an internal standard (for chemical shifting) at ambient temperature. Other conditions used were data points 32 K, lock material methanol-d4 (solvent), spectral width 8000.0 Hz, pulse width 12.6 µsec (pulse angle 90°), pulse delay time 2 sec, and number of FID accumulation 32. The total time for acquisition was approximate 3 minutes.

Prior to quantification, FT-NMR spectra were recorded for pure DIBP and TCE in methanol-d4 prior to analysis of standard and sample solution. The assignment of various peak in different chemicals were carried out and the assignment of all the peak are shown in Table 1.

Table 1: FT-NMR peak position of various organic components.

Compound	Peak Assignments
TCE	6.4 ppm singlet
Methanol-d4	3.3 ppm singlet, 4.8 ppm singlet (for residual moisture in solvent)
DIBP	0.9 ppm doublet (12 proton), 2.0 ppm multiplet (2 proton), 4.0 ppm doublet (4 proton), 7.6 ppm multiplet (2 proton) and 7.7 ppm multiplet (2 proton)

2.2. Procedure

2.2.1. Preparation of stock solution

Standard stock solution-A containing 150 mg of DIBP in 1.5 ml of methanol-d4; and standard stock solution-B containing 200 mg of TCE in 3 ml of methanol-d4 were prepared. Methanol-d4 used for further dilution for preparation of standard solutions. Stock solution C was prepared by taking TCE in methanol d-4, where the concentration of TCE is 20 mg in 600 µL solution.

2.2.2. Preparation of standard solutions

Standard solutions of varied amount of DIBP and constant amount of TCE were prepared using stock solution A and B with solvent methanol-d4. The amount of various solutions and concentration of various standard solutions were shown in Table 2.

Table 2. Standard solution preparation and composition

Stock Solution A (μL)	Stock Solution-B (μL)	Solvent (μL) (Methanol-d4)	Total Volume (μL)	Amount of DIBP (mg)	Amount of TCE (mg)
10	300	290	600	1	20
20	300	280	600	2	20
40	300	260	600	4	20
60	300	240	600	6	20
100	300	200	600	10	20
150	300	150	600	15	20
200	300	100	600	20	20
300	300	0	600	30	20

2.2.3. Preparation of sample solution

Optimum amount of catalyst (~ 50 mg) in 600 μL of sample stock solution C was used for estimation quantitative estimation.

3. Results and Discussion

MgCl$_2$ supported titanium catalyst system is complex mixture of MgCl$_2$, TiCl$_4$ and organic species as internal electron donors (MgCl$_2$.xID.yTiCl$_4$). Quantification of internal electron donor can be done by extraction of donor in organic solvents. In solid-state, donor compounds are coordinated with support matrix [13], however in methanolic solution catalyst components disintegrate to give soluble componenet mixture (Equation 1):

$$MgCl_2.xID.yTiCl_4 + MeOH \rightarrow MgCl_2.aMeOH + Ti(OMe)_b(Cl)_c + HCl + ID \qquad (1)$$

In methanol organic donor is not in coordinated form as confirmed by proton NMR (Fig.1) and 13C NMR. The peaks of pure organic component (DIBP) and the catalyst solution shows similar chemical shift. It indicates the presence of donor component in free form in methanol solution. The proton NMR of catalyst in methanol shows peaks of organic component present in catalyst (Fig.1). The intensity of the spectrum peaks is directly dependant on the amount of proton present in the sample. Hence the peak intensity of the NMR is utilized. It was clearly indicated in Table 1 that the no peak is overlapped among TCE, DIBP and solvent, hence fixed amount of TCE can be used as standard for unknown composition analysis through NMR and peak at 0.9 ppm of DIBP can be used for the quantification of the compound.

3.1. Calibration Curve

Standard solutions were subjected to proton NMR experiments. The relative intensity of internal standard (TCE) and the peak (0.9 ppm) of DIBP are shown in Table 3. The amount of TCE was constant in all sample, hence the intensity of TCE peak was also taken as constant for all the samples.

The calibration curve was prepared by taking intensity of methyl proton intensity of DIBP v/s amount of DIBP in solution and shown in Fig.2. It was observed that the curve is linear and follows the intensity and amount relationship of proton in FT-NMR spectroscopy.
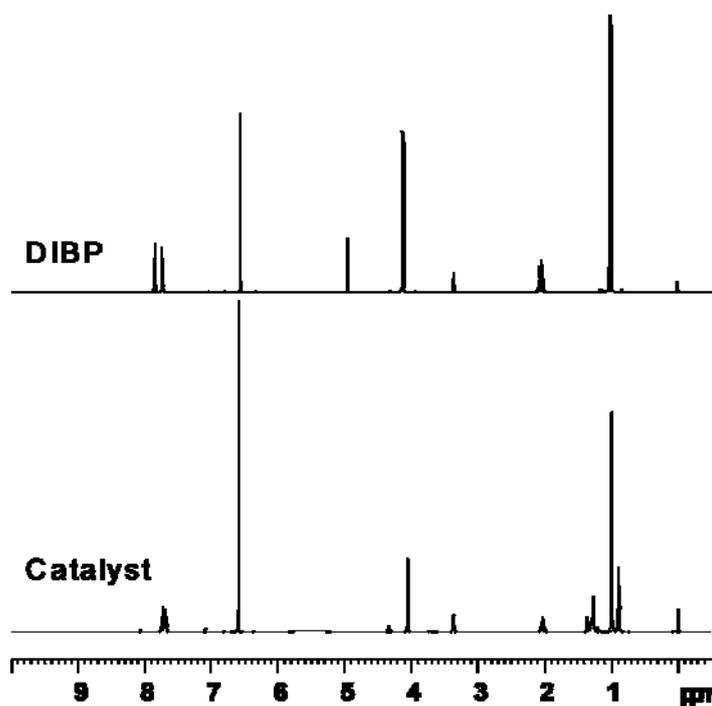
Fig.1. Proton NMR spectrum of DIBP and catalyst in methanol-d4

The regression analysis (Equation 2) using the method of least squares was made for slope (m), intercept (c) and correlation obtained from different concentrations and the results are summarized in Table 3.

$$Y = mx + c \tag{2}$$

Where regression equation slope m= 21.088 and correlation coefficient $R^2 = 0.998$.

Table 3: Intensity of peaks in standard solutions

Standard Sample	Weight (mg)		Relative Intensity of Peak	
	TCE	DIBP	TCE	DIBP
0	20	0	100	0.0
1	20	1	100	18.5
2	20	2	100	38.6
3	20	4	100	75.9
4	20	6	100	111.7
5	20	10	100	201.8
6	20	15	100	315.9
7	20	20	100	415.4
8	20	30	100	644.6

Various catalysts with different DIBP concentration were synthesized and checked for the concentration by NMR method. The calibration curve (Fig.2) was used to estimate the DIBP amount in catalysts. The data indicated in Table 4 represents the results in weight percent of DIBP in the catalysts. HPLC results confirm the same amount in the catalyst. It is clearly understood from the results that the quantification using NMR spectroscopy is giving

similar results like chromatography; hence the proposed approach gives quantitative results for DIBP estimation in catalysts.

Table 4. Amount of DIBP in various catalysts

Catalyst sample	Relative Intensity of DIBP peak	Amount of DIBP (mg)	Wt. of catalyst (mg)	Wt. in catalyst by NMR (%)	Wt. in catalyst by HPLC (%)
Cat-1	199.43	9.45	50.2	18.8	18.7
Cat-2	148.13	7.02	50.6	13.9	13.9
Cat-3	135.39	6.41	50.7	12.7	12.9
Cat-4	20.28	0.96	50.8	1.8	1.6
Cat-5	12.90	0.61	56.9	1.1	1.1
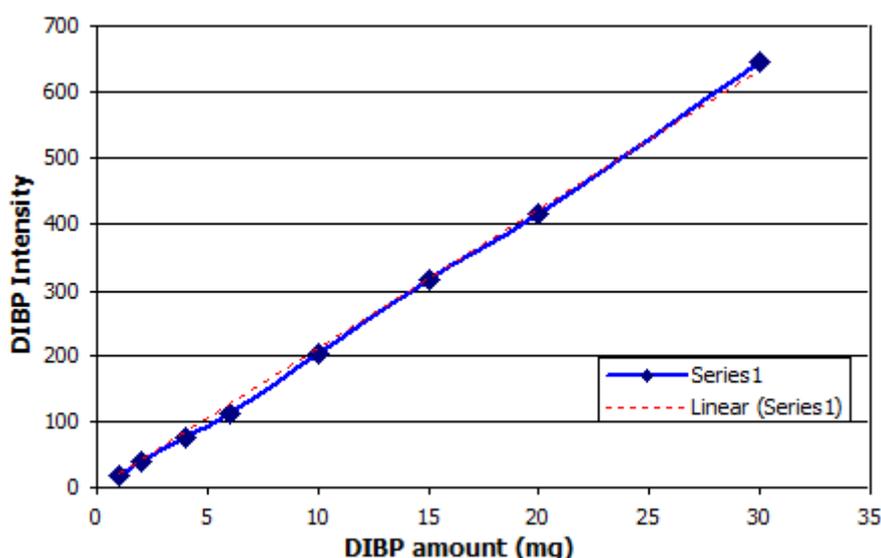
Fig.2. Calibration curve (DIBP amount v/s peak intensity)

4. Conclusion

The developed method based on proton NMR is simple, sensitive and accurate for estimation of internal donor in supported titanium catalyst system. The method is demonstrated for the estimation of diisobutyl phthalate in supported catalyst. The overall approach can be used as alternative method for qualitative and quantitative estimation of organic electron donors in catalysts.

Acknowledgement

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