



Homogeneous and supported bis(imino)pyridyl vanadium(III) catalysts

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ABSTRACT

Bis(imino)pyridyl vanadium(III) complexes have been synthesized and characterized by NMR, FT-IR and UV–vis spectroscopy. The activation reaction of these complexes in solution with methylalumoxane (MAO) was followed by UV–vis spectroscopy.

The reactions of the complexes with the surface of silica were monitored by FT-IR spectroscopy. The resulting materials were activated with MAO or triisobutylaluminium (TIBA) and the catalytic systems were evaluated in the polymerization of ethylene. Characterization of the catalysts was accomplished by elemental analysis and by UV–vis spectroscopy. The effects caused by the nature of the support in the fixing reaction of the complex, as well as the catalytic activities of the resulting materials compared with those of the molecular precursors, are presented and discussed.

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1. Introduction

The catalytic polymerization of simple olefins, such as ethylene or propylene, by single-site organometallic catalysts has been the dominion of the early transition metals. Metallocene catalysts can readily be tuned by ligand modifications and continue to be a subject of research effort [1]. Since the early works of Brookhart and coworkers [2] and Gibson and coworkers [3], the application of non-metallocene pyridinediimine complexes of iron(II) in this field has been adopted rapidly in recent years [4]. The knowledge gained in this area has been used to obtain new specific ligands or new complexes based on metals other than iron or cobalt.

Preliminary studies on homogeneous Ziegler–Natta catalysts are based on combinations of simple vanadium complexes and alkylaluminium co-catalysts [5], which are used to produce syndiotactic polypropylene or copolymers of ethylene and α -olefins. These catalysts suffer from a relatively fast decay in the activity, probably due to the reduction of the active V(III) or V(IV) species to inactive V(II) complexes. Nowadays, V(acac)₃ is widely used to produce elastomer polymers [6].

In parallel with the development of bis(imino)pyridyl (BIP) systems based on iron or cobalt, a few studies concerning the behaviour of analogous V(III) complexes have been carried out [7–9]. In

fact, [2,6-bis{1-(2,6-diisopropylphenylimino)-ethyl}pyridine vanadium(III)] (**1**) has been structurally and spectroscopically characterized and it is an active catalyst precursor for the polymerization of ethylene after activation with methylalumoxane (MAO) (611 kgPE[molV h^{-1}], at 20 bar, 413 K and a 600:1 Al:V ratio; 186 kgPE[molV h^{-1}], at 1 bar, 323 K and a 100:1 Al:V ratio). In contrast with iron analogues, participation of the ligand in the reactivity of the catalyst was proposed. Other similar complexes have recently been studied as pre-catalysts for ethylene oligomerization, but characterization by NMR was not carried out [9]. Semikolenova and coworkers [10] recently found that aluminium trialkyls (e.g. triisobutylaluminium, TIBA) are also effective co-catalysts for bis(imino)pyridyl iron complexes.

There are dozens of references on supported catalysts based on iron complexes with bis(imino)pyridine ligands and these cover both purely academic and industrial research [11]. By supporting these complexes on partially dehydroxylated silica or alumina [12–14], these materials can be activated with TIBA to obtain stable ethylene polymerization catalysts. On the evidence of IR spectroscopy, a reduced loading of the complexes on the support was proposed as a result of strong interactions between surface hydroxyl groups and high density electronic regions of the complex, with no significant changes in the structure of the latter.

As with molecular vanadium complexes, supported catalysts based on these precursors have been less widely studied than their counterpart iron complexes. Good results have been obtained by supporting vanadium complexes on a 15% (w/w) MAO-modified silica (300–500 kgPE[molV h^{-1}], at 23 bar, 353 K, and using

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additional TIBA as co-catalyst [15]. Similar results were found on using MgCl_2 -modified $\text{AlR}_n(\text{OEt})_{3-n}$ [16]. This approach is expected to give catalysts that provide polymers with higher molecular weights than those obtained using homogeneous systems and also with a narrower weight distribution. These results can be explained on the basis of the presence of a single type of active centre, which have been described as being similar to those proposed in solution.

Our research efforts to develop new catalysts based on early transition metals [17–20] allowed us to synthesize and study the reactivity of vanadium(III) bis(imino)pyridine complexes as homogeneous or supported catalysts in the polymerization of ethylene. In this paper we report the characterization of complexes of the type $[\text{VCl}_3\{\text{C}_5\text{H}_3\text{N}[(\text{MeC}=\text{N})(\text{C}_6\text{R}_3\text{H}_2)]_2\}]$ [$\text{R}_3 = i\text{Pr}_2\text{H}$ (**1**), Me_2H (**2**), Me_3 (**3**)] by NMR, FT-IR and UV–vis spectroscopy. These complexes were then supported on dehydroxylated silica and silica–MAO and the new materials were characterized. In addition, the behaviour of these compounds was compared with that of the molecular precursors. The reactivity of these complexes and supported materials towards co-catalysts such as MAO or TIBA was also studied. Some catalytic tests in the polymerization of ethylene are also presented.

2. Experimental

2.1. Materials

Grace Davison XPO 2407 silica ($200\text{ m}^2\text{ g}^{-1}$, particle average size: $70\ \mu\text{m}$, pore size distribution: 6–30 nm, pore volume: 1.7 ml/g) was partially dehydroxylated under vacuum (10^{-2} mmHg) for 16 h at 523 K [$\text{SiO}_2(\mathbf{523})$], cooled and stored under dry nitrogen. Diacetylpyridine, anilines, $[\text{VCl}_3(\text{THF})_3]$ and $[\text{FeCl}_2(\text{H}_2\text{O})_4]$ (Aldrich), ethylene (Alphagaz), AliBu_3 (TIBA, 1 M in hexanes, Aldrich) and methylalumoxane (MAO, 10% in toluene, Aldrich) were used without further purification. Toluene (SDS) was distilled over sodium under a dry nitrogen atmosphere. In a similar manner, CH_2Cl_2 (SDS) was distilled over P_2O_5 . Complexes **1**, **2**, **2b** and **3** were prepared as described in the literature [9].

2.2. Supported catalyst preparation

The supported catalysts were prepared under an inert atmosphere using Schlenk techniques and a glove-box. A solution of the complex in CH_2Cl_2 (30 mL, 0.1 mmol/g SiO_2) was added to partially dehydroxylated silica (1 g) and the mixture was stirred at 298 K for 30 min. The slurries were filtered through fritted discs and washed 10 times with CH_2Cl_2 (20 mL) until a colourless filtrate was obtained. The resulting solids were dried under vacuum at 298 K for 16 h. In the case of MAO-modified silica [SiO_2 –MAO], SiO_2 (**523**) (1 g) was treated with a toluene MAO solution (10 mL MAO/g SiO_2). The mixture was stirred at 298 K for 1 h and dried in vacuo at 333 K. The resulting material was impregnated with the complexes as described above.

2.3. Characterization

The infrared spectra of ligands and complexes were recorded on a BRUKER TENSOR 27 FT-IR spectrophotometer in the form of Nujol mulls. A total of 32 scans were typically accumulated for each spectrum (resolution 2 cm^{-1}). For *in situ* experiments on supported catalysts, an infrared cell equipped with CaF_2 windows was used. The samples consisted of ca. 20 mg of silica pressed into a self-supported disc of 1 cm diameter. The samples were partially dehydroxylated at the desired temperature for 16 h. The complex support process was performed using a 10^{-2} M solution in dichloromethane. The samples were washed with dichloromethane and dried in vacuo at 298 K until no further change was observed. The FT-IR analyses were repeated on three different samples in

order to ensure reproducibility. NMR analyses were performed in CD_2Cl_2 using a Varian INOVA 500 spectrometer with a sweep width of 100 kHz and 100 scans. UV–vis analyses were performed using a Shimadzu UV-2501PC spectrophotometer. The soluble complexes were dissolved in dry toluene and placed in special cells under dry nitrogen (1.0 cm path length). The solid samples were suspended in Nujol to form a slurry. The absorption spectra were recorded between 190 nm and 900 nm and toluene or Nujol was used as a reference. Elemental analyses were determined at the Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany). The molecular weights of polyethylenes (M_n) were measured using an AVS-300 viscometer in decahydronaphthalene at $408 \pm 0.1\text{ K}$ and calculated from $[\eta]$ according to Eq. (1).

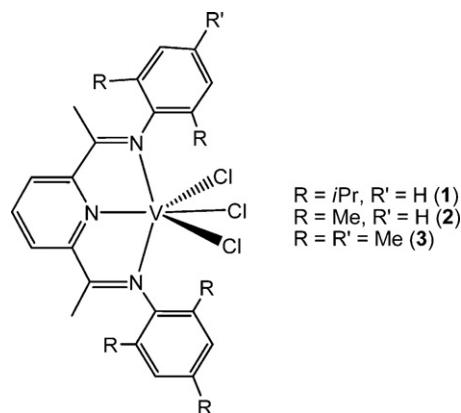
$$[\eta] = 2.3 \times 10^{-4} M_n^{0.82} \quad (1)$$

2.4. Polymerization tests

Polymerizations were carried out in a 250-mL glass reactor using toluene as a solvent. Catalysts ($6 \times 10^{-6}\text{ mol}$ for the homogeneous reactions and approximately 100 mg for the heterogeneous ones) were treated with the appropriate quantity of a solution of co-catalyst for 15 min to obtain an Al:V ratio of 500. In the case of MAO-modified silica, additional co-catalyst was added (see text). Toluene and the activated catalyst (final volume ca. 100 mL) were introduced, in this order, into the reactor and thermostated at the desired temperature. Nitrogen was removed and a continuous flow of ethylene (1.5 bar) was introduced for 30 min. The reaction was then quenched by the addition of acidified methanol. The polymer was collected, washed with methanol and dried under vacuum at room temperature for 24 h.

3. Results and discussion

Complexes **1**, **2** and **3** (Scheme 1) (and the complex **2b**, based on Fe(II), as an analogous complex for the sake of comparison) were synthesized using literature procedures and were characterized by spectroscopic methods. Although complex **1** has already been characterized by ^1H NMR spectroscopy [8], the NMR characterization of these complexes was performed using CD_2Cl_2 as a solvent and a large sweep width, since the spectra display very shielded and deshielded peaks, which correspond to the pyridine and iminic methyl groups, respectively, due to the proximity to the paramagnetic centre (Fig. 1). The ^1H NMR spectrum of **1** in CD_2Cl_2 shows the following notable peaks: at -5.0 ppm , the *meta* protons of pyridine; at 2.0 ppm , the corresponding *para* proton; at 2.6 ppm and 0.8 ppm , the inequivalent methyl groups of the isopropyl moieties; at 3.9 ppm , the methinic protons of the isopropyl groups; at



Scheme 1. Bis(imino)pyridine vanadium (III) complexes.

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