



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

Javier Romero, Fernando Carrillo-Hermosilla*, Antonio Antiñolo*, Antonio Otero

Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Campus Universitario de Ciudad Real, 13071-Ciudad Real, Spain

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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

* Corresponding authors. Tel.: +34 26295300; fax: +34 26295318.
E-mail addresses: Fernando.Carrillo@uclm.es (F. Carrillo-Hermosilla),
Antonio.Antinolo@uclm.es (A. Antiñolo).

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).

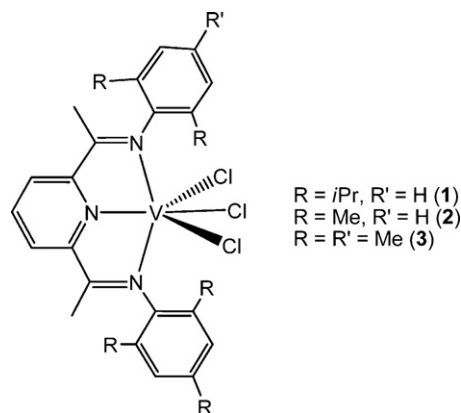
$$[\eta] = 2.3 \times 10^{-4} M_n^{0.82} \quad (1)$$

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.

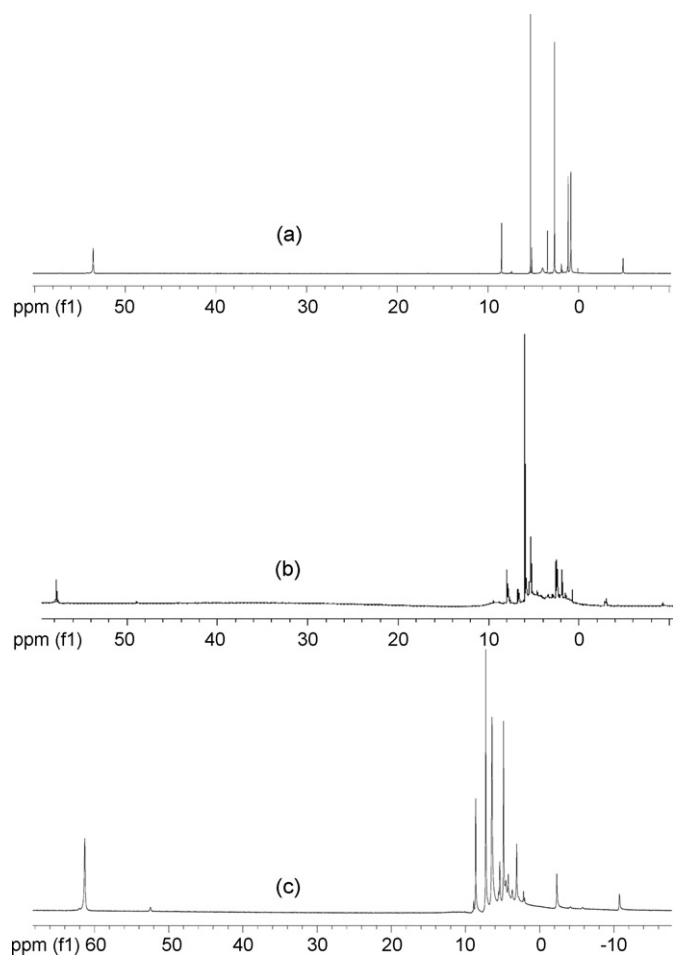


Fig. 1. ^1H NMR spectra of bis(imino)pyridine vanadium (III) complexes, in CD_2Cl_2 : (a) complex **1**; (b) complex **2**; (c) complex **3**.

5.1 ppm, the *para* protons of the phenyl groups; at 8.5 ppm, the corresponding *meta* protons; and, finally, at 53.8 ppm, the imino methyl groups. The ^1H NMR spectrum of **2** in CD_2Cl_2 shows the following notable peaks: at -10.5 ppm, the *para* proton of the pyridine; at -3.9 ppm, the corresponding *meta* protons; at 5.6 ppm, the *ortho* methyl groups; at 6.4 ppm, the corresponding *para* proton of the phenyl groups; finally, at 59.3 ppm, the imino methyl groups. Finally, the ^1H NMR spectrum of **3** in CD_2Cl_2 shows the following notable peaks: at -10.7 ppm, the *para* proton of the pyridine; at -2.3 ppm, the corresponding *meta* protons; at 6.4 ppm, the *para* methyl groups; at 7.2 ppm, the *ortho* methyl groups; at 8.6 ppm, the *meta* protons of the phenyl groups; finally, at 61.3 ppm, the imino methyl groups.

The complexes were also characterized by FT-IR spectroscopy and it was observed that the frequency of the vibration of the imino groups of the ligands, which appear near to 1640 cm^{-1} , move to 1575 cm^{-1} after coordination to the metal centre. This shift to lower wavenumber upon complexation is consistent with observations made for other 2,6-bis(imino)pyridine metal complexes [21].

The UV–vis spectra of the vanadium complexes were recorded along with those of the activated solutions. Changes between the UV–vis spectra of the ligands and the corresponding complexes can clearly be observed (Fig. 2). All of the complexes reported in this paper are intensely coloured. For example, solutions of the bis(imino)pyridine vanadium trichloride complexes are violet (**1**) or greenish (**2**, **3**). All of the complexes, as well as the free ligand, show two characteristic absorptions in the UV region between 270 nm and 440 nm and these are due to ligand-based transitions

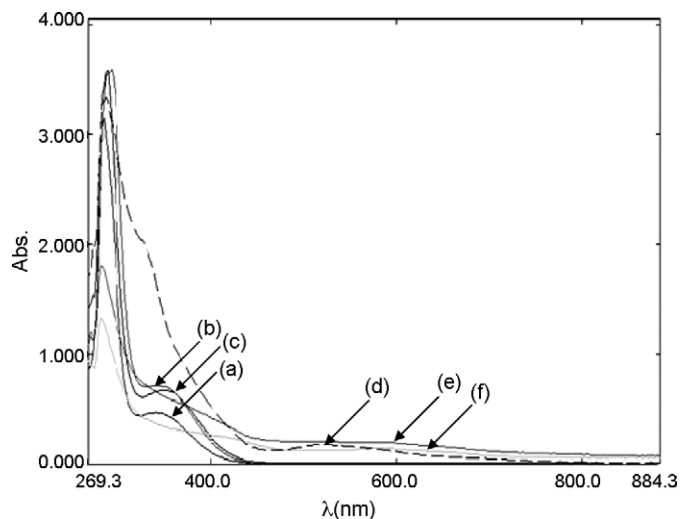


Fig. 2. UV–vis spectra of (a) BIP ligand of complex **1**; (b) BIP ligand of complex **2**; (c) BIP ligand of complex **3**; (d) complex **1**; (e) complex **2**; (f) complex **3**.

(π – π^*). In the visible region, the vanadium complexes **1**, **2** and **3** display a broad absorption at around 570 nm, which is probably due to metal-to-ligand charge transfer (MLCT). The differences observed for complex **1** in comparison to the similar complexes **2** and **3** indicate the influence that the bulky isopropyl groups have on the properties of this complex.

UV–vis spectroscopic studies of MAO-activated olefin polymerization systems have been carried out previously for metallocenes and α -diimine nickel catalysts [22]. Activation of the vanadium pre-catalysts with the co-catalyst MAO gives rise to colour changes in these materials.

Addition, at a very low ratio (100:1 Al:V), of MAO activator to toluene solutions of the pre-catalysts gave rise to an orange solution in all cases. These solutions all display similar UV–vis spectra (Fig. 3), which shows that, for complexes **2** and **3**, similar active species appear to be generated upon activation with MAO. Complex **1** shows an additional band at 830 nm. The use of higher Al:V ratios gave rise to essentially identical spectra. Gambarotta and coworkers [7] proposed the direct involvement of the ligand in the reactivity of the metal centre as the key to understanding the high activity of these catalytic systems, with the first step in the activation being the alkylation of the pyridine ring that transforms the initial coordination complex into a covalent transition metal amide. This process

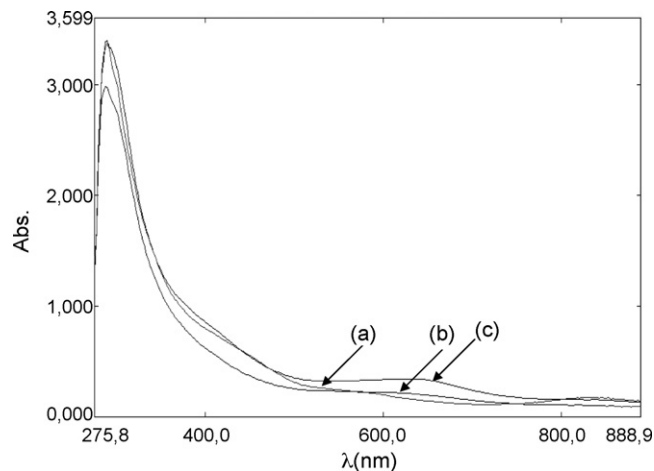
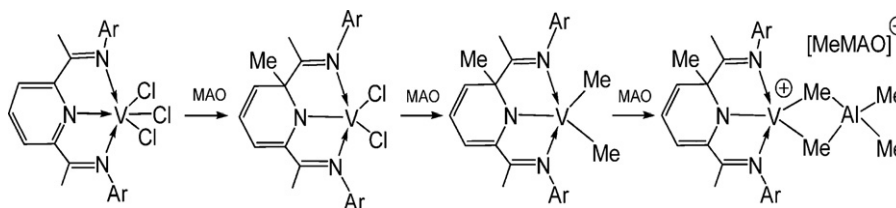


Fig. 3. UV–vis spectra of (a) complex **1** after MAO addition (Al:V = 100); (b) complex **2** after MAO addition (Al:V = 100); (c) complex **3** after MAO addition (Al:V = 100).



Scheme 2. Proposed activation mechanism for bis(imino)pyridine vanadium (III) complexes by MAO.

is accompanied by a decrease in the coordination number of the metal centre to give a more stable catalyst (see **Scheme 2**).

In our conditions, these systems exhibited high activity in ethylene polymerization (**Table 1**) at low pressure, in the presence of MAO, similar or higher to the previous reported activities of complex **1** [7,8], but only oily residues were found when TIBA was used as the co-catalyst. A significant influence of the Al:V ratio was not found (i.e., complex **2** shows an activity of $467 \text{ kgPE}[\text{molV h}]^{-1}$ at an Al:V of 500, and $403 \text{ kgPE}[\text{molV h}]^{-1}$ at an Al:V ratio of 100), but a significant decay in the activity was found for these vanadium complexes during the course of the polymerization (i.e., complex **2** shows an activity of $1800 \text{ kgPE}[\text{molV h}]^{-1}$ after 5 min of reaction and $477 \text{ kgPE}[\text{molV h}]^{-1}$ after 30 min).

It has been proposed that ion-pairs are formed for analogous iron(II) systems in the presence of MAO [23]. The formation of cation-like species' $[(\text{BIP})\text{Fe}(\text{II})(\mu\text{-Me})(\mu\text{-Cl})(\text{AlMe}_2)]^+[\text{Me-MAO}]^-$ and $[(\text{BIP})\text{Fe}(\text{II})(\mu\text{-Me})_2(\text{AlMe}_2)]^+[\text{Me-MAO}]^-$, which are similar to those accepted for activated group 4 metallocenes, was proposed on the basis of NMR experiments. The assumption that an ion-pair is also present for vanadium(III) complexes (**Scheme 2**) at an Al:V ratio of 100 or higher could be substantiated by the UV-vis spectra of **3**, activated by MAO and recorded in different solvents with different dielectric constant, as shown in **Fig. 4**. A shift in the main band to higher wavelength was observed on increasing the polarity of the solvent, thus indicating an increase in the effective positive charge on the metal centre—a situation that facilitates electron transfer from the metal to the more attractive remaining coordinated BIP ligand.

Table 1

Polymerization conditions are as follows: $P=1.5 \text{ bar}$; $6 \times 10^{-6} \text{ mol}$ of complex or approximately 100 mg of supported catalyst; $[\text{Al}]/[\text{M}]$ approximately 500; $T=343 \text{ K}$; solvent = toluene (total volume 100 mL); time = 30 min.

Entry no.	Catalyst	Co-catalyst	Activity ($\text{kgPE}[\text{mol}(\text{M})\text{h}]^{-1}$)	M_n (g mol^{-1})
1	1	MAO	533	53,400
2	1	TIBA	Oily residues	n.d. ^a
3	2	MAO	477	55,600
4	2	TIBA	Oily residues	n.d. ^a
5	2b	MAO	443	n.d. ^a
6	3	MAO	643	59,800
7	3	TIBA	Oily residues	n.d. ^a
8	1 . $[\text{SiO}_2\text{-MAO}]$	MAO	185	95,600
9	1 . $[\text{SiO}_2\text{-MAO}]$	TIBA	96	n.d. ^a
10	2 . $[\text{SiO}_2\text{-MAO}]$	MAO	205	86,000
11	2 . $[\text{SiO}_2\text{-MAO}]$	TIBA	319	88,500
12	3 . $[\text{SiO}_2\text{-MAO}]$	MAO	212	56,900
13	3 . $[\text{SiO}_2\text{-MAO}]$	TIBA	578	62,300
14	1 . $[\text{SiO}_2(523)]$	MAO	106	n.d. ^a
15	1 . $[\text{SiO}_2(523)]$	TIBA	Traces	n.d. ^a
16	2 . $[\text{SiO}_2(523)]$	MAO	Traces	n.d. ^a
17	2 . $[\text{SiO}_2(523)]$	TIBA	200	92,000
18	3 . $[\text{SiO}_2(523)]$	MAO	Traces	n.d. ^a
19	3 . $[\text{SiO}_2(523)]$	TIBA	243	66,500

^a Not determined.

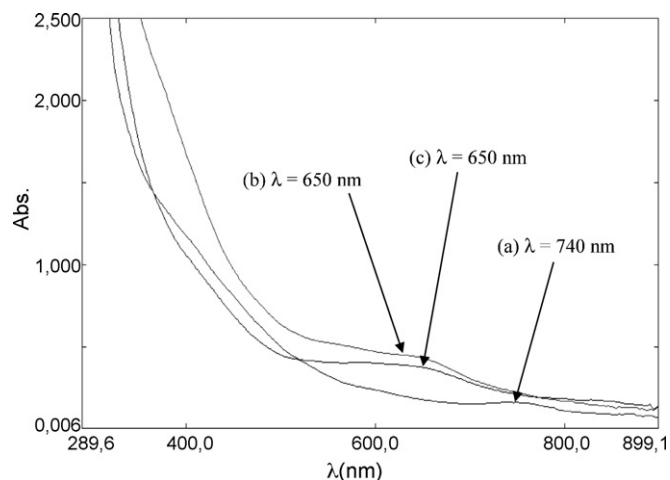


Fig. 4. UV-vis spectra of complex **3** after activation with MAO (Al:V=100): (a) in CH_2Cl_2 ; (b) in toluene; (c) in hexanes.

Vanadium complexes were supported on partially dehydroxylated silica pre-treated with MAO to give light brown solids. Analysis of the supported catalysts by UV-vis spectroscopy was performed in Nujol (**Fig. 5**). A band can be seen at 260 nm, corresponding to the $\text{SiO}_2\text{-MAO}$ support, with broad shoulders at 290 nm and 420 nm, assigned to the supported complex. In contrast to the solution spectra, bands were not observed near to 600 nm (attributed to active species) and neither were the characteristic starting complex bands near to 570 nm for the supported forms. Data for the activities in ethylene polymerization of the supported catalysts are given in **Table 1**. MAO-modified silica-supported systems did not exhibit activity without additional MAO or TIBA co-catalyst. The values are in the order of the previously described systems [15],

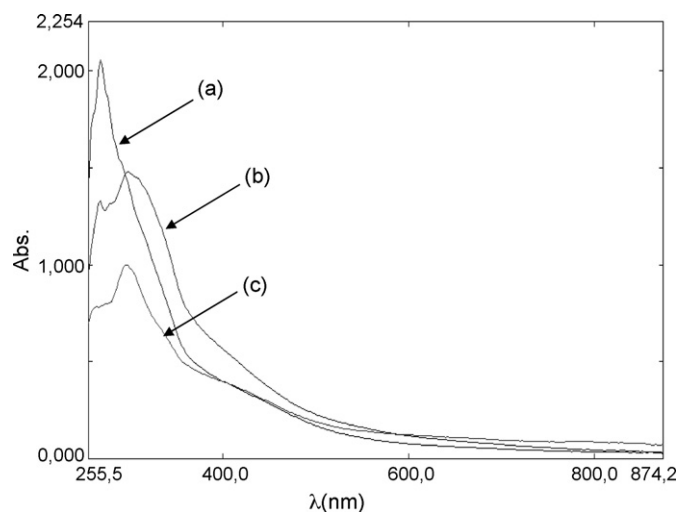
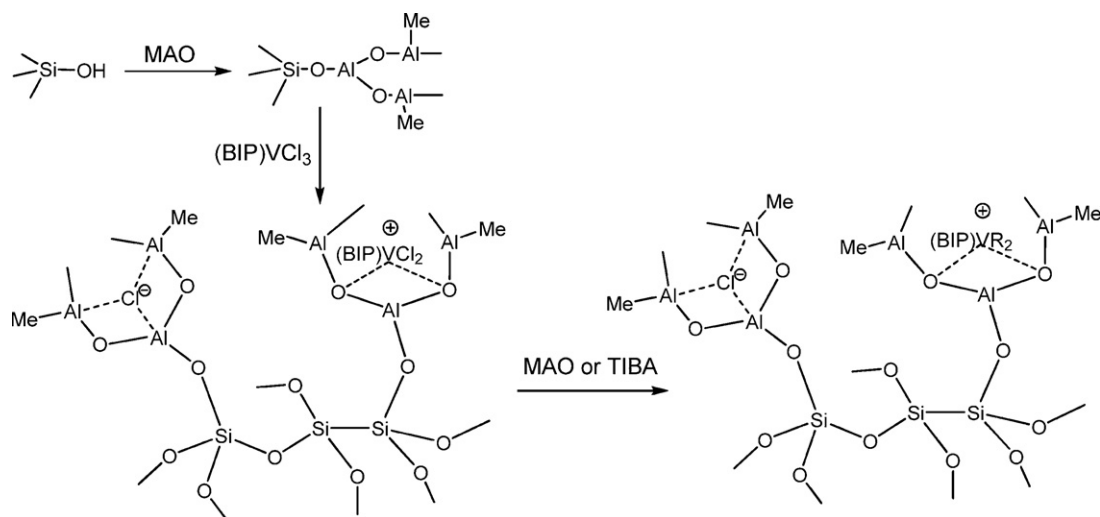


Fig. 5. UV-vis spectra of (a) complex **1** supported on $\text{SiO}_2\text{-MAO}$; (b) complex **2** supported on $\text{SiO}_2\text{-MAO}$; (c) complex **3** supported on $\text{SiO}_2\text{-MAO}$.



Scheme 3. Possible surface active species on MAO-modified silica.

even at lower pressure. This finding probably indicates that these supported systems are different from the original complexes, but the surface species' are not the final active ones and require an alkylating agent such as MAO or TIBA (Scheme 3).

The vanadium complexes were supported directly on unmodified partially dehydroxylated silica in an analogous manner to that described elsewhere [12,14] for iron(II) complexes. The systems described are active catalysts even on using TIBA as a co-catalyst. BIP or chlorine ligands. When vanadium(III) complexes were supported on partially dehydroxylated silica, $\text{SiO}_2(523)$, solids with similar colours to those of the molecular precursors were obtained. A UV–vis analysis of the supported catalysts was performed in Nujol (Fig. 6). As far as the SiO_2 –MAO supported catalysts are concerned, the disappearance of the characteristic high wavelength of the original complexes was observed and new broad signals appeared on the broad band of the silica. These new signals are assigned to the supported complexes.

The amount of vanadium complex fixed onto the silica from dichloromethane solutions was determined by increasing the metal contents in the initial solutions. The resulting adsorption isotherm for complex **2**, at 298 K, is shown in Fig. 7. The curve shows that the metal loading approaches a saturation limit near to 1.5% and this

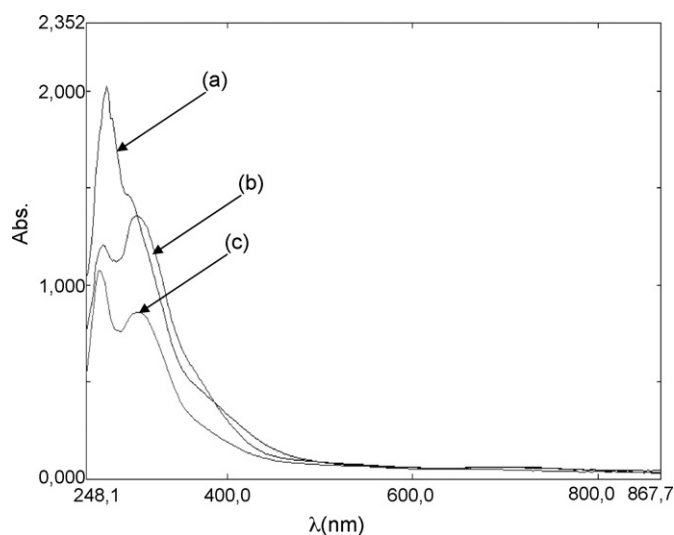


Fig. 6. UV–vis spectra of (a) complex **1** supported on $\text{SiO}_2(523)$; (b) complex **2** supported on $\text{SiO}_2(523)$; (c) complex **3** supported on $\text{SiO}_2(523)$.

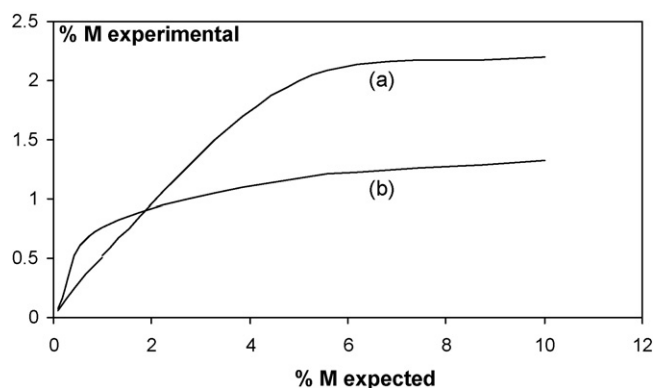


Fig. 7. Adsorption isotherms of (a) complex **2a** and (b) complex **2**.

is typical of a chemisorption process. The limit was very low, even when a large excess of complex was used. For comparison, iron(II) complex **2b** was also studied and it was found that an upper limit can be obtained for this complex. This finding could be due to the different geometry and electronic distribution of vanadium(III) and iron(II) complexes.

The vanadium loading of the samples prepared to give a theoretical value of 0.5% in metal was obtained from solutions of the three complexes and the results are summarized in Table 2. The values obtained for analogous samples supported on SiO_2 –MAO are also given. It can be seen that a better fixation can be achieved by using unmodified silica, probably due to the higher availability of fixing hydroxyl groups.

The IR spectra shown in Fig. 7 correspond to the reaction between a dichloromethane solution of **2** and the surface of unmodified partially dehydroxylated silica after removal of the solvent (see Section 2). The spectrum of silica preheated at 523 K [$\text{SiO}_2(523)$] has

Table 2
%V loading for supported catalysts.

Catalyst	%V
1.[SiO_2 –MAO]	0.27
2.[SiO_2 –MAO]	0.33
3.[SiO_2 –MAO]	0.23
1.[$\text{SiO}_2(523)$]	0.39
2.[$\text{SiO}_2(523)$]	0.40
3.[$\text{SiO}_2(523)$]	0.36

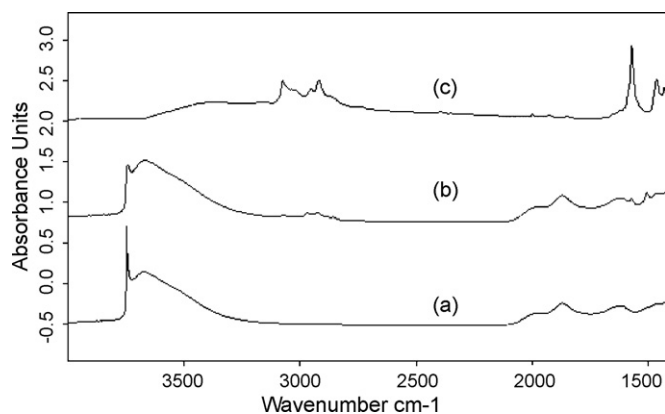


Fig. 8. FT-IR spectra of (a) $\text{SiO}_2(250)$, (b) after complex **2** fixation, (c) complex **2**.

a sharp band at 3747 cm^{-1} , assigned to isolated OH groups, with a broad shoulder at 3670 cm^{-1} , which can be attributed to silanols that are perturbed due to hydrogen bonding contacts (Fig. 8a). Bands at 1866 cm^{-1} and 1640 cm^{-1} are combinations and overtone bands of Si–O network bonds. After contact with the complex solution and removal of the solvent (Fig. 8b), new bands can be seen in the 3000 cm^{-1} and 1500 cm^{-1} regions and these correspond to stretching and bending modes of BIP ligands. The OH groups that were initially isolated are now partially perturbed, generating broad $\nu(\text{OH})$ bands at lower frequencies, probably due to an interaction through hydrogen bonding, as proposed for analogous iron complexes and other catalysts based on the support of active complexes on the surface of partially dehydroxylated silica [12,14,24]. A comparison between the spectra of the free complex (Fig. 9a) and the supported form (Fig. 9b) is represented in Fig. 8 after subtraction of the support spectrum. After contact with the surface, slight modifications of the stretching bands can be observed. In addition, a significant new band appears at 1510 cm^{-1} , close to the band assigned to the imino groups of the original complex, thus indicating some interaction between some of these groups and the surface of the silica (Scheme 4).

Data for the activity in ethylene polymerization of the $\text{SiO}_2(523)$ supported catalysts are given in Table 1. The values are in the order of the previously described systems [15], even at lower pressure. In contrast with the SiO_2 –MAO supported systems, the effectiveness of the co-catalyst depends on the nature of the original complex. In fact, similar complexes **2** and **3** are active after the simple addition of TIBA, whereas supported complex **1** requires MAO before showing moderate activity, thus indicating different surface active species in

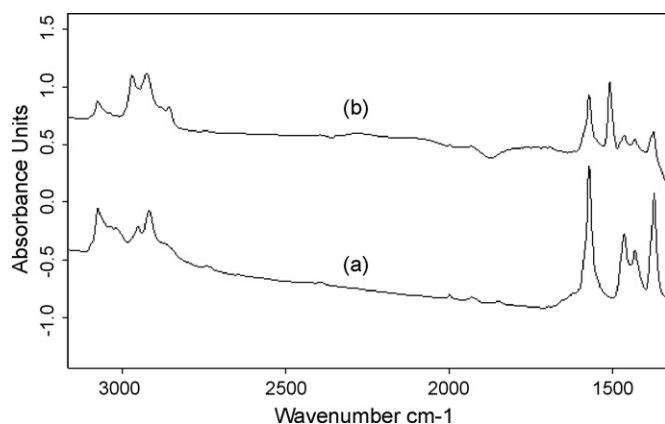
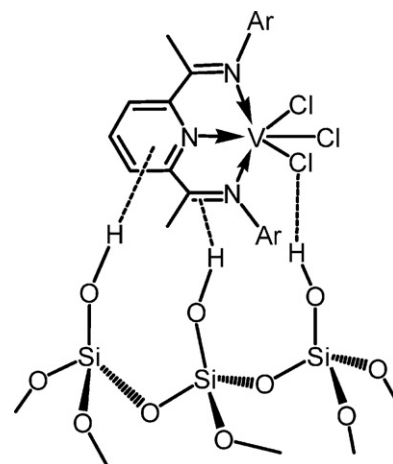


Fig. 9. FT-IR spectra of (a) complex **2** and (b) complex **2** supported on $\text{SiO}_2(523)$, after subtraction of the support spectrum.



Scheme 4. Possible surface species on partially dehydroxylated silica.

these systems. This situation is analogous to the slightly different UV–vis spectra in solution.

4. Conclusions

Bis(imino)pyridyl vanadium(III) complexes were synthesized and characterized by ^1H NMR, FT-IR and UV–vis spectroscopy. The resulting materials were studied as pre-catalysts in the polymerization of ethylene. On the basis of the UV–vis spectra, after the addition of MAO, we propose the formation of ion-pair-like systems to be the active forms of these catalysts.

When these complexes were supported on MAO-modified silica, additional co-catalyst was needed in order to obtain active species. In contrast, active catalysts can be obtained by supporting these compounds on partially dehydroxylated silica, with some of these systems active even in presence of a simple trialkylaluminum compound such as TIBA.

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