

# Polymerization of Ethylene by Supported Zirconium Alkoxide Complex

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Received 16 June 2009; accepted 25 March 2010

DOI 10.1002/app.32552

Published online 3 June 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Dichlorobis(3-hydroxy-2-methyl-4-pyrone) Zr(IV) was grafted onto different inorganic supports, namely SiO<sub>2</sub>, MAO-modified SiO<sub>2</sub>, MCM-41, Al<sub>2</sub>O<sub>3</sub>, and MgO. The resulting supported catalysts were shown to be active in ethylene polymerization using methylaluminoxane (MAO) as the catalyst. Catalysts were characterized by Rutherford Backscattering Spectrometry (RBS)

and nitrogen adsorption method. The highest catalyst activities were observed for the zirconium complex supported on MCM-41. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1561–1566, 2010

**Key words:** non-metallocene catalyst; polyethylene; polymerization; supported catalysts; zirconium alkoxide

## INTRODUCTION

Currently there is a great interest in the discovery and development of new families of catalysts for the polymerization of  $\alpha$ -olefins aiming at a larger control on the properties of the resulting polymers. More recently, new generations of non-metallocene catalysts have been proposed in the literature.<sup>1</sup> The aim is to develop new systems (the so-called post-metallocene catalysts), which besides not being covered by patents, are capable to afford further improvements in polymer product properties and production flexibility. In spite of metallocene catalysts being very versatile, the non-metallocene single-site catalysts usually provide several advantages, among them their chemical synthesis being much more straightforward in many cases than that of the metallocene. Therefore, new post-metallocene complexes bearing bidentate alkoxide ligands have been constantly proposed in the literature.<sup>2–5</sup> Sobota and coworkers synthesized the complex dichlorobis(3-hydroxy-2-methyl-4-pyrone)Ti(IV) and evaluated its catalytic activity in ethylene polymerization, showing that the ligand could be a good alternative to cyclopentadienyl ring.<sup>6</sup>

The catalytic activity of Sobota's titanium complex has been investigated by our research group. The

homogenous complex was tested in ethylene polymerization under different experimental conditions like temperature, Al/Ti ratio, and concentration of the catalyst.<sup>7</sup> In a preview study, the titanium complex was also supported on different inorganic matrix. It is worth mentioning that the potential industrial applicability of this kind of catalytic system depends on its capacity to be supported, allowing its use in industrial Ziegler-Natta plants. All supported system showed catalytic activity at ethylene polymerization using MAO as the cocatalyst. Many of them were even more active than the homogeneous counterparts, differing from metallocenes, in which a loss of ca. 10% of its catalyst activity is observed in the supported systems. The complex supported on SiO<sub>2</sub>, 948, MCM-41 (Mobil Compositom of Matter) and Al<sub>2</sub>O<sub>3</sub> presented very high catalytic activities.<sup>8</sup> The analog complex bearing zirconium as metallic center, dichlorobis(3-hydroxy-2-methyl-4-pyrone)Zr(IV) complex, was synthesized and it was tested on ethylene polymerization, using MAO or TIBA as the cocatalyst. The complex was very active for this kind of reaction, producing polymers with high molecular weight.<sup>9</sup>

In the present work, dichlorobis(3-hydroxy-2-methyl-4-pyrone) zirconium(IV) complex was grafted on different inorganic carriers, namely SiO<sub>2</sub>, MAO-modified SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, and MCM-41. The choice of these supports is based on the fact that they present different textures (surface area and pore diameter) as well as surface sites bearing different acid/base characteristics. The resulting systems were evaluated in ethylene polymerization, having methylaluminoxane (MAO) as the cocatalyst.

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Contract grant sponsors: CNPq, CAPES, PRONEX/FAPERGS.

## EXPERIMENTAL

### General procedures

All experiments were performed under argon atmosphere using Schlenk-type glassware. Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium and benzophenone. Dichloromethane was dried by refluxing over phosphorus pentoxide. The synthesis of the zirconium complex is described elsewhere.<sup>9</sup> MCM-41 was synthesized according to the literature.<sup>10</sup> The supports, Al<sub>2</sub>O<sub>3</sub> (Inlab), MgO (Riedel), and MCM-41 were activated under vacuum ( $<10^{-4}$  mbar) for 16 h at 723 K. SiO<sub>2</sub> 956 (Grace) was activated at 383 K, and the MAO-modified SiO<sub>2</sub> (23 wt % Al, Witco) was used without treatment. The support was then cooled to room temperature under dynamic vacuum and stored under dried argon. MAO (Witco, 5.2 wt % Al in toluene solution) was employed as received.

### Preparation of the supported catalysts

Supported catalysts were prepared by the grafting method.<sup>11</sup> In a typical experiment, for instance, a [dichlorobis(3-hydroxy-2-methyl-4-pyrone)zirconium(IV)] toluene solution corresponding to 0.5 wt % Zr/support was added to the pretreated support (1.0 g), and the resulting slurry was stirred for 1 h at 353 K and then filtered through a fritted disk. The resulting solids were washed with 15 aliquots (2.0 cm<sup>3</sup>) of toluene and dried under vacuum for 4 h. For the determination of the adsorption isotherm of the grafted complex, solutions containing initial concentrations corresponding to 0.1 and 2.0 wt % Zr/SiO<sub>2</sub> were grafted on the support.

### Characterization of the supported catalyst

Zirconium loadings in catalysts were determined by Rutherford Backscattering Spectrometry (RBS) using He<sup>+</sup> beams of 2.0 MeV incident on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. The method is based on the determination of the number and the energy of the detected particles which are elastically scattered in the Coulombic field of the atomic nuclei in the target. In this study, the Zr/M (M = Si, Mg, or Al) atomic ratio was determined from the heights of the signals corresponding to each of the elements in the spectra and converted to wt % Zr/support. For an introduction to the method and applications of this technique the reader is referred elsewhere.<sup>12</sup> Specific surface area was determined by the BET method from N<sub>2</sub> adsorption data at 77 K using a Gemini 2375 (Micromeritics). The samples were outgassed at 60°C for 6 h before measuring the nitrogen adsorption.

### Leaching test

In a typical experiment, a known amount of Zr/SiO<sub>2</sub> supported catalyst (SiO<sub>2</sub> activated at 383 K) corresponding to 3 μmol of Zr was suspended in 0.3 dm<sup>3</sup> of toluene with MAO (Al/Ti = 2500) under argon. The system was stirred for 1 h at 313 K and then filtered through a fritted disk. The filtered solution was transferred into the reactor under argon. The polymerization reactions were carried out under 1.6 bar of ethylene pressure, at 313 K for 1 h. Acidified (HCl) ethanol was used to quench the process.

### Polymerization

Ethylene polymerizations were performed in 0.3 L of toluene in a 1.0 L Pyrex glass reactor connected to a constant temperature circulator, equipped with a mechanical stirrer, and inlets for argon and the monomer. MAO was used as the cocatalyst at Al/Zr molar ratio of 2500. For each experiment, 1 μmol or 10 μmol of Zr catalyst was suspended in toluene and transferred into the reactor under argon. The polymerizations were performed at 1.6 bar pressure of ethylene at different temperatures for 60 min. The reagents were introduced in the reactor in the following order: solvent, cocatalyst, ethylene, and catalyst. Acidified (HCl) ethanol was used to quench the processes, and reaction products were separated by filtration, washed with distilled water, and finally dried under reduced pressure at room temperature.

### Polymer characterization

The melting points ( $T_m$ ) and crystallinities ( $X_c$ ) of the polymers were determined on using a differential scanning calorimeter (Perkin Elmer, DSC-4), at a heating and cooling rate of 10°C min<sup>-1</sup> in the temperature range 30–160°C. The heating cycle was performed twice, but only the results of the second scan are reported. Molar masses and molar mass distributions were measured by high temperature gel permeation (GPC) using a 150 C Waters instrument, equipped with a differential refractometer, and HT Styragel columns (HT3, HT4, and HT6). 1,2,4-Trichlorobenzene was used as mobile phase at a flow rate of 1 mL min<sup>-1</sup>. The analysis was performed at 135°C.

## RESULTS AND DISCUSSION

The dichlorobis(3-hydroxy-2-methyl-4-pyrone)zirconium(IV) complex was supported on different inorganic carriers bearing different texture properties and potential immobilization sites with different acid/basic characteristics. Considering zirconium complex structure, we assumed that the mechanism

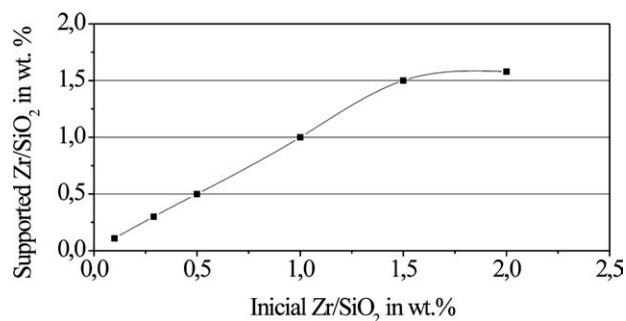


Figure 1 Adsorption isotherm of the silica.

of supporting catalyst on inorganic matrix is similar that one widely described for metallocene complexes. In spite of dealing with supports, which may differ not only on textural properties (surface area and pore diameter), but also on acid or basic properties, all of them (excepting MAO-modified silica) bear OH groups on their surface, which may promote the reaction with the chloride from the catalyst. Thus, the interaction between catalyst and support's surface may take place through a covalent reaction. In the case of MAO-modified silica, the generated surface species might be more complex, due to the no-totally clarified MAO structure. The presence of alkyl group may cause the formation of the active species (cationic species) already on the support's surface.

Initially, the zirconium complex was grafted on silica, considering that this inorganic support has been frequently used due to its surface area and porosity, good mechanical properties, relative inert characteristics, and stability under processing conditions.<sup>13,14</sup>

To determine the surface saturation of this complex on silica, the adsorption isotherm was determined considering the immobilized zirconium percentage. Solutions with concentrations corresponding to values between 0.1 and 2.0 wt % Zr/SiO<sub>2</sub> were contacted to silica. The washing step with toluene after a given contact time guaranteed that the grafted amount belong to a chemically bound species on the support. The immobilization reactions

on silica, treated at 110°C were done at 25°C. Figure 1 shows the adsorption isotherm.

According to Figure 1, the saturation of the silica surface occurs around 1.5 wt % Zr/SiO<sub>2</sub>. Comparing with metallocenes, this value is relatively high because grafted zirconocene content was found, for instance, 0.57 and 0.45 wt % Zr/SiO<sub>2</sub> for silica pre-treated at 110 and 450°C, respectively. Moreover, silica supports bearing different textural properties or prepared by different methods (aerogel, xerogel, for instance) afforded lower grafted Zr content.<sup>11,15</sup> It was already discussed in the literature that the number of OH groups on a support surface limits the amount of immobilized catalyst and it decreases with the raise of the treatment temperature during the thermal activation of the support: from 4.5 OH nm<sup>-2</sup> at 25°C to around 1.7 OH nm<sup>-2</sup> at 450°C.<sup>16,17</sup> Thus, the low temperature used in the present work for thermal activation of the silica could have guaranteed a support with a large number of OH groups and therefore, with a great number of potential sites for the complex immobilization. It is worth nothing that almost all the complex present in the toluene solution seemed to have been immobilized on the silica surface for contents below 1.5 wt % Zr/SiO<sub>2</sub>. Such behavior suggested a strong interaction between the catalyst and the surface.

The zirconium complex was also supported on MAO-modified SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, and MCM-41. Table I presents some textural properties of the same supports. The employed concentration was 0.5 wt % Zr/support, because in the case of silica such metal content is far from the saturation level.

According to Table I, all the amount of metal complex seems to be immobilized, independently of the surface area, exception to MgO. The lower fixation observed in the case of MgO can be related to its much lower surface area. Furthermore, for this supported catalyst system, a reduction in 35% of the surface area was observed. For the rest of the catalysts, very small changes were observed between before and after the grafting reaction suggesting that catalyst might be immobilized in the outermost opening of the pores, not blocking them, probably due to steric effect played by the complex geometry.

TABLE I  
Grafted Zirconium Content on Different Supported Catalysts and Textural Characteristics

Support	Zr/support (wt %)	S <sub>BET</sub> (support) (m <sup>2</sup> /g)	S <sub>BET</sub> (catalyst) (m <sup>2</sup> /g)	D <sub>p</sub> (support) (Å)	D <sub>p</sub> (catalyst) (Å)
SiO <sub>2</sub>	0.5	210	199	270	160
MAO-modified SiO <sub>2</sub>	0.5	–	–	–	–
MCM-41	0.5	1271	1170	29	29
MgO	0.4	105	70	–	69
Al <sub>2</sub> O <sub>3</sub>	0.5	137	117	64	68

S<sub>BET</sub>, surface area determined by the BET method; D<sub>p</sub>, pore diameter.

**TABLE II**  
**Catalyst Activity of Zirconium Complex and Properties of the Resulting Polymers**

System	Catalytic activity <sup>a</sup>	$T_m$ (°C)	$M_w$ ( $10^5$ g/mol)	$M_w/M_n$
Homogeneous	45.0	134	5.67	3.7
MCM-41	45.6	131	3.39	2.9
MgO	12.5	125	1.62	1.4
SiO <sub>2</sub>	25.5	125	5.28	5.9
MAO-modified silica	22.3	124	1.36	1.5
Al <sub>2</sub> O <sub>3</sub>	16.3	129	1.32	1.6
Homogeneous <sup>b</sup>	180.0	135	1.62	1.9
MCM-41 <sup>b</sup>	132.7	127	i	–
MgO <sup>b</sup>	42.9	132	i	–

Polymerization conditions: 60°C, Al/Zr = 2500; [Zr] = 1  $\mu$ mol.

<sup>a</sup> Expressed in kg PE/(mol Zrh atm).

<sup>b</sup> [Zr] = 10  $\mu$ mol; i = insoluble.

According to Table I, only in the case of silica, that has the largest pore diameter, a sensible reduction was observed after the grafting reaction.

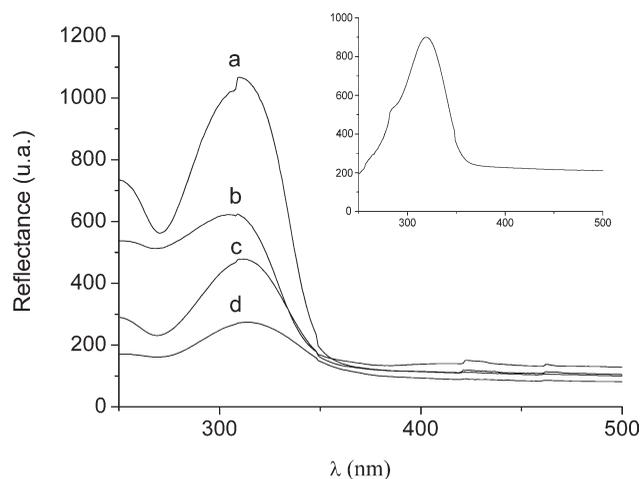
A leaching test was carried out to check if the MAO cocatalyst would be capable of removing the supported catalyst from the support's surface to the solution. In all tested systems, no activity was observed in the supernatant liquid, suggesting the metal was indeed fixed on support.

Table II shows the catalytic activity of the supported systems in the polymerization of ethylene. For comparative reasons, data from the homogeneous system were also included.

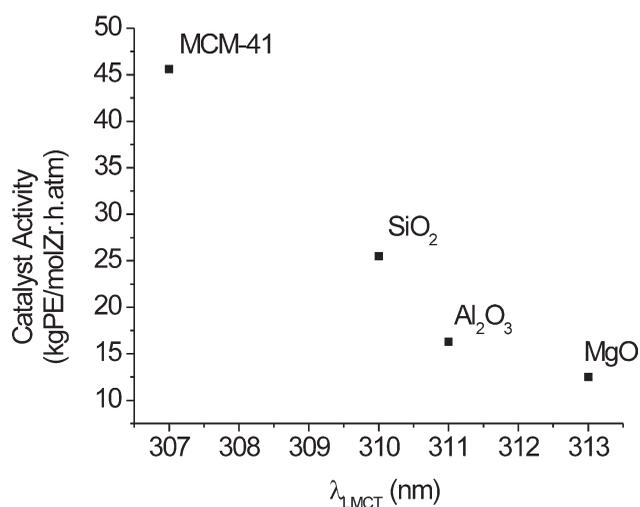
The catalytic systems showed moderate activity, in accordance with observations done on other similar complexes based on ligands bearing alkoxide donors.<sup>1</sup> According to Table II, when 1  $\mu$ mol of zirconium complex was used, the catalytic activity of the homogeneous system was higher than of the supported systems, excepting MCM-41. In general, the activity of the supported metallocene catalysts is reduced in comparison to those of homogeneous systems.<sup>11</sup> Many reasons have been attributed to this reduction in activity, such as the generation of a small fraction of active species of the total of the grafted content and the steric effect played by the support surface itself, which plays the role of a huge ligand.<sup>18</sup> However, as previously mentioned, in the case of the complex supported on MCM-41 there was no catalytic activity reduction comparing with the homogeneous system. Similar behavior has been reported for the titanium analogous complex: it was observed that the catalytic activity was twice more than that of the homogeneous system when the complex was supported on MCM-41.<sup>8</sup> In the same experiment conditions, better activities were obtained when it used 10  $\mu$ mol of the zirconium complex.

Active species produced during polymerization reaction have been studied by the UV-Vis spectroscopy

aiming at understanding the nature of the catalyst species.<sup>19</sup> Measurements by diffuse reflectance spectroscopy (UV-Visible/DRS) of the supported zirconium complex on different inorganic matrix, showed a hypsochromic displacement of the band assigned to the ligand to metal charge transfer (LMCT) band when the catalyst is supported on the matrix (Fig. 2). This effect suggest an increase in electronic density at the zirconium atom.<sup>20</sup> The reason why this effect occurs could not be explained by the simple replacement of a chlorine atom by an oxygen from the support, because in this case, the effect should be the opposite, due to the higher electronegativity of the oxygen. The support should be considerate as a whole and there is probably other interactions, support-catalyst that are contributing to increase the electronic density of the metal. Further studies should be done to understand better the reason of this effect.



**Figure 2** UV-Visible diffuse reflectance spectra of supported zirconium pyrone catalyst: (a) SiO<sub>2</sub>, (b) MCM-41, (c) Al<sub>2</sub>O<sub>3</sub>, and (d) MgO. (Inset: homogeneous system).



**Figure 3** Relationship between UV-Vis absorption band of the supported catalysts and their corresponding catalyst activity in ethylene polymerization.

The relationship between the hypsochromic displacement of LMCT band in the UV-visible spectrum and catalytic activity of the supported systems is shown in Figure 3. It is clear that when the electronic density at the zirconium increases, the catalytic activity also increases. Similar results were reported for silica-supported metallocene catalysts, in which was observed that activity to increase with an increase in the electron density of zirconium atom.<sup>21–23</sup> This effect can be easily explained by a lower interaction of the olefin with the metal facilitating the monomer insertion. Furthermore, on the previous cyclic voltammetry studies involving the complex zirconium complex, we have observed the necessity of the coordination of ethylene to stabilize the zirconium active species created by the reaction of complex with MAO.<sup>7</sup> These results suggesting that the species actives need a higher electronic density at zirconium atom and it is like that in catalyst-supported systems, the inorganic matrix would be contributing for to stabilize the metallic center.

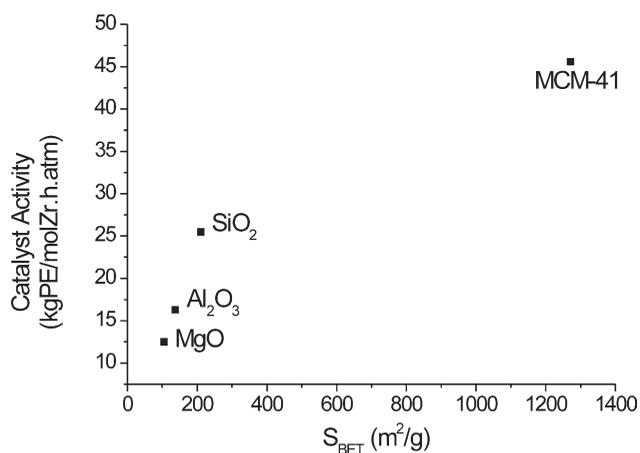
Under the same experimental conditions, the lowest catalytic activities were obtained for MgO (basic support) and Al<sub>2</sub>O<sub>3</sub> (acid support), comparing to SiO<sub>2</sub> and MCM-41. The results suggest that the nature of support surface might impinging some effect on the catalyst activity of the supported species. Similar results have been observed for the other non-metallocene supported catalysts.<sup>24</sup> One cannot neglect that textural properties of the support (surface specific area, pore diameter, surface roughness) may also affect catalyst activity. For instance, MgO is a very low surface area support and this influence not only the distribution of catalyst center (the more agglomerate the surface species, the lower the catalyst activity) but also the access of the monomer to

the catalyst center. Conversely, the high surface specific surface area of MCM-41 may contribute to the higher catalyst activity observed for the system generated on this support.

The behavior shown in Figure 3 can also be resulting from the textural characteristics of the supports. Figure 4 correlates specific area ( $S_{\text{BET}}$ ) with catalyst activities.

According to Figure 4, an increase in specific area of the support affords an increase in catalyst activity. More spaced catalyst species on a support's surface (clearly, obtained in a support of larger surface area), make easier the access of the monomer or of the cocatalyst to the catalyst sites. MCM-41 seems to be the best support for these catalytic systems, probably due to its high surface area and also its higher organization.

The polymers obtained with the homogeneous and supported MCM-41 systems presented typical melting temperatures ( $T_m$ ) of high density polyethylene. The others supported systems presented lower values of  $T_m$ . Lower values of molecular weight observed in the case of polymers produced by the supported systems suggests that the support itself might not be contributing in the stabilization of the catalytic species during polymeric chain growth. A higher  $M_w$  value observed in the case of SiO<sub>2</sub> can be related to the pore diameter variation detected after the grafting reaction. In such supported systems, part of the catalyst species might be grafted within the pores, which in turn might be less prone to chain termination reaction. Similar observations have been recently reported in the literature dealing with silica-based supports and grafted metallocenes.<sup>25</sup> The molecular weight distributions remained between 1.5 and 5.9. The broad distribution is probably related to the presence of several types of surfaces sites in support. SiO<sub>2</sub> and MAO-modified silica showed the



**Figure 4** Relationship between surface area ( $S_{\text{BET}}$ ) of the supports and catalytic activity of the resulting supported catalysts.

similar activities, but can be observed in Table II that the molar mass distribution of polymers can be controlled by modifying the structure of silica surface.

### CONCLUSIONS

The complex dichlorobis(3-hydroxy-2-methyl-4-pyrone)zirconium(IV) presented catalytic activity at ethylene polymerization in homogeneous medium and supported on different inorganic matrix. Catalyst activity was shown to be dependent on the nature of the support. MCM-41 was shown to be the best support, probably due to its high surface area. On the other hand, supports as silica, with high pore diameter values, and therefore, can engender the grafting reaction within the pore surface, seems to guarantee a better stabilization of the surface species, which engenders polymers with higher molecular weight.

The authors thank Dr. Raúl Quijada, Departamento de Ingeniería Química-Universidad de Chile, for GPC measurements.

### References

- Kaminsky, W.; Sperber, O.; Werner, R. *Coord Chem Rev* 2006, 250, 110.
- Sobota, P. *Coord Chem Rev* 2004, 248, 1047.
- Gueta-Neyroud, T.; Tumanskii, B.; Kapon, M.; Eisen, M. S. *Macromolecules* 2007, 40, 5261.
- Gornshtein, F.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* 2007, 3, 497.
- Fim, F. C.; Machado, T.; Sá, D. S.; Livotto, P. R.; Rocha, Z. N.; Basso, N. R. S.; Galland, G. B. *J Polym Sci A Polym Chem* 2008, 46, 3830.
- Sobota, P.; Przybylak, K.; Utko, J.; Jerzykiewicz, L. B.; Pombeiro, A. J. L.; Silva, M. F. C. G.; Szczegot, K. *Chem Eur J* 2001, 7, 951.
- Basso, N. R. S.; Greco, P. P.; Carone, C. L. P.; Livotto, P. R.; Simplicio, L. M. T.; Rocha, Z. N.; Galland, G. B.; Santos, J. H. Z. *J Mol Catal A Chem* 2007, 267, 129.
- Greco, P.; Brambilla, R.; Einloft, S.; Stedile, F. C.; Santos, J. H. Z.; Galland, G. B.; Basso, N. R. S. *J Mol Catal A Chem* 2005, 240, 61.
- Carone, C.; Lima, V.; Albuquerque, F.; Nunes, P.; Lemos, C.; Santos, J. H. Z.; Galland, G. B.; Stedile, F. C.; Einloft, S.; Basso, N. R. S. *J Mol Catal A Chem* 2004, 208, 285.
- Kim, J. M.; Kwak, L. H.; Jun, S.; Ryoo, R. *J Phys Chem* 1995, 99, 16742.
- Santos, J. H. Z.; Krug, C.; Rosa, M. B.; Stedile, F. C.; Dupont, J.; Forte, M. C. *J Mol Catal A Chem* 1999, 139, 199.
- Stedile, F. C.; Santos, J. H. Z. *Phys Stat Sol (a)* 1999, 173, 123.
- Collins, S.; Kelly, W. M.; Holden, D. A. *Macromolecules* 1992, 25, 1780.
- Chien, J. C. W.; He, D. J. *Polym Sci A Polym Chem* 1991, 29, 1603.
- Silveira, F.; Pires, G. P.; Petry, C. F.; Pozebon, D.; Stedile, F. C.; Santos, J. H. Z.; Rigacci, A. *J Mol Catal A Chem* 2007, 265, 167.
- Ciesla, U.; Schuth, F. *Microporous Mesoporous Mater* 1999, 27, 131.
- Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.
- Muñoz-Escalona, A.; Méndez, L.; Sancho, J.; Lafuente, P.; Peña, B.; Micheils, W.; Hidalgo, G.; Marnitez-Núñez, M. F. In *Metallorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer: Heidelberg, 1999; pp 381–396.
- Gil, M. P.; Santos, J. H. Z.; Casagrande, O. L. *J Mol Catal A Chem* 2004, 209, 163.
- Coevoet, D.; Cramail, H.; Deffeux, A. *Macromol Chem Phys* 1998, 199, 1451.
- Franceschini, F. C.; Tavares, T. T. R.; Bianchini, D.; Alves, M. C. M.; Ferreira, M. L.; Santos, J. H. Z. *J Appl Polym* 2009, 112, 563.
- Fish, A.; Cardozo, N.; Secchi, A.; Stedile, F.; Silveira, N.; Santos, J. *J Non-Cryst Solids* 2008, 354, 3973.
- Silveira, F.; Alves, M. C. M.; Stedile, F. C.; Pergher, S. B. C.; Santos, J. H. Z. *Macromol React Eng* 2009, 3, 139.
- Casagrande, A. C. A.; Tavares, T. T. R.; Kuhn, M. C. A.; Casagrande, O. L.; Santos, J. H. Z.; Teranishi, T. *J Mol Catal A Chem* 2004, 212, 267.
- Silveira, F.; Alves, M. C. M.; Stedile, F. C.; Pergher, S. B.; Rigacci, A.; Santos, J. H. Z. *J Mol Catal A Chem* 2009, 298, 40.