MOF-Supported Selective Ethylene Dimerization Single-Site Catalysts through One-Pot Postsynthetic Modification

Jerome Canivet,* Sonia Aguado, Yves Schuurman, and David Farrusseng

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), Université Lyon 1-CNRS 2, Av. Albert Einstein, F-69626 Villeurbanne, France

Ⓢ *Supporting Information*

ABSTRACT: The one-pot postfunctionalization allows anchoring a molecular nickel complex into a mesoporous metal−organic framework (Ni@(Fe)MIL-101). It is generating a very active and reusable catalyst for the liquid-phase ethylene dimerization to selectively form 1-butene. Higher selectivity for 1-butene is found using the Ni@(Fe)MIL-101 catalyst than reported for molecular nickel diimino complexes.

The understanding of mechanisms involved in heterogeneously catalyzed reactions is a challenge continuously addressed for several decades. One of the main approaches consists of the "heterogenization" of molecular catalysts, or in other words, the insertion of a metallo complex into or onto a solid by different methods, also known as surface organometallic chemistry.[1] The role of the support is analogous to that of a rigid ligand in the corresponding molecular complex. However, the grafting of molecular catalysts on the surface of solid oxides has often led to a loss of activity due to detrimental interactions with the support or to mutual deactivation between too close sites.[2] Generally, the design of isolated single active sites at the support surface is thus essential.[3] This is specially the case for the development of heterogeneous catalyst for olefin polymerization which remains a challenge because of a drastic loss of the activity upon grafting on support.[4]

In this study, we show that Metal−Organic Frameworks (MOF) constitute an appealing new and relevant platform for the seeding of supported single site catalysts.[5] They offer the key advantages of a high site density combined with well-defined and isolated sites for the anchoring of catalytic species. Compared to amorphous silica which has nonhomogeneously scattered OH groups and an average site density from two to six per square nanometer,[6] the crystalline MOF (Cr) MIL-101 exhibits 3 to 4 Cr atoms/nm^2, equivalent to the density of the organic ligand, homogeneously distributed in a well-ordered framework.[7] This represents an efficient compromise between high site density and site isolation.

The postsynthetic modification, comprehensively reviewed by Cohen and co-workers,[8] is a powerful tool for obtaining highly sophisticated functionalized structures. It consists of the introduction of functionalities after framework synthesis and allows the preparation of MOF-supported organometallics following various methods.[9] However the postsynthetically introduced coordinating moieties could interact with metal nodes, as demonstrated by Banerjee et al. on the (Cr) MIL-

101.[10] In addition, the use of metal salts as precursors could also lead to pore blocking with metal aggregates[11] which may also contribute to unselective catalytic activity.[12]

We report here the first one-pot postsynthetic grafting of a nickel-based organometallic catalyst within a MOF framework under mild conditions, preventing the interactions of the organic graft with the metal nodes and the encapsulation of metal particles (Scheme 1). This method allows the rapid

Scheme 1. One-Pot Synthesis of the MOF-Anchored Nickel Complex Ni@(Fe)MIL-101[a]

10% functionnalization: 10Ni@(Fe)MIL-101
30% functionnalization: 30Ni@(Fe)MIL-101
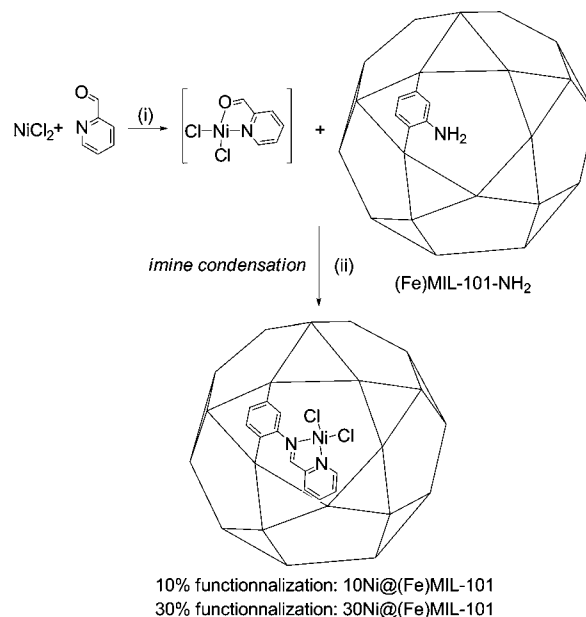
[a]Conditions: (i) NiCl$_2$ and PyCHO in MeOH ; (ii) (Fe)MIL-101-NH$_2$ (∼0.3−1 equiv -NH$_2$) stirred at room temperature.

preparation of a MOF-based catalyst whose activity and selectivity are demonstrated for the selective ethylene dimerization to give the corresponding alpha olefin (1-butene) in liquid phase.

The (Fe)MIL-101-NH$_2$, which is isostructural to the (Cr)MIL-101[7a,13] and is formed by trimeric iron(III) octahedral clusters linked by 2-aminoterephthalate ligands, is selected as starting platform.[14] Related to its giant-pore MOF

parent, the (Fe)MIL-101-NH$_2$ can be considered as an ideal candidate thanks to its high pore volume which is able to accommodate organometallic species as well as substrates and to amino groups on its walls acting as a starting platform for postsynthetic functionalization. According to data reported on MIL-101 structure, the amino site density can be evaluated to four per square nanometer.[7]

With the perspective to anchor organometallics into MOF cavities, we aim to create N,N-chelating centers from 2-aminoterephthalate (BDC-NH$_2$) by the reaction with 2-pyridine carboxaldehyde (PyCHO) to give the corresponding pyridine methanimino group (BDC-NCHPy) onto the MOF walls. To avoid the competitive N-coordination of the pyridyl moieties to the coordinatively unsaturated metal sites of the (Fe)MIL-101-NH$_2$,[7c,14a] we first N-coordinated the pyridyl to the desired nickel salt to allow the formyl group of the compound formed to react with the amino at the MOF walls (Scheme 1).

The imine condensation occurs in the presence of the Ni(PyCHO)Cl$_2$ methanolic solution to directly form the diimino nickel complex anchored into the MOF (Scheme 1). Indeed, we can expect that the coordination of the nickel to the formyl group could increase its electrophilicity and thus could favor its condensation to the weak nucleophilic amino groups at the MOF walls. The postmodification yield is measured from ^{1}H NMR spectra after sample digestion in DCl/D$_2$O/dmso-d_6 (Supporting Information). The condensation proceeds with 10% yield when 1 equiv of PyCHO/NiCl$_2$ per -NH$_2$ moiety on the MOF is used and the suspension stirred for 24 h at room temperature, to give 10Ni@(Fe)MIL-101. Following the same methodology, 30Ni@(Fe)MIL-101, in which 30% of the amino groups are converted, is obtained using 3 equiv of PyCHO/ NiCl$_2$ for 72 h. The appearance in the NMR spectra of new typical aromatic signals at 8.1, 8.6, and 8.8 ppm, corresponding to pyridyl and imine CH protons, indicates the efficient functionalization of the BDC aromatic ring.

Unfortunately, the paramagnetic effect of iron(III) leads to a low resolution and a peak broadening in NMR spectra. Nevertheless, by using a very low concentration of the MOF in the deuterated solution and consequently a high number of scans, workable spectra are obtained.

PXRD analysis confirms the structural integrity of the materials after the functionalization step (Supporting Information). Additionally, the EDX analyses show the atomic ratios Ni:Cl to be 1:2 which confirm that all the nickel remains in its dichloride form. Combining NMR and EDX data, we can formulate the desolvated functionalized solids as Fe$_3$OCl(BDC-NH$_2$)$_{2.7}$[(BDC-NCHPy)NiCl$_2$]$_{0.3}$ for 10Ni@(Fe)MIL-101 and Fe$_3$OCl(BDC-NH$_2$)$_2$[(BDC-NCHPy)NiCl$_2$] for 30Ni@(Fe)-MIL-101 (Supporting Information).

As expected and according to the N$_2$ adsorption isotherms, the postmodification is accompanied by a decrease of the BET surface, from 1884 m^2·g^{-1} for (Fe)MIL-101-NH$_2$ to 1110 m^2·g^{-1} for 10Ni@(Fe)MIL-101 and 155 m^2·g^{-1} for 30Ni@(Fe)MIL-101 (Supporting Information). The very low value reported for 30Ni@(Fe)MIL-101 is due to the presence of a high number of nickel species inside the MOF pores. Indeed, the actual complex loading onto the solid is approximately 10 and 33 nickel complexes per MOF cage for 10Ni@(Fe)MIL-101 and 30Ni@(Fe)MIL-101, respectively.[7]

The continuous increase in the commercial demands for C$_4$ to C$_8$ linear α-olefins, which are promising co-monomers of linear low-density polyethylenes, presses forward the develop-

ment of efficient catalysts for ethylene oligomerization. Major commercial processes, such as SHOP from Shell or Alfabutol from IFP-New Energy, are based on homogeneous catalysts.[15] Moreover, the development of heterogeneous catalysts for olefin polymerization, especially alpha isomers, remains a challenge because the grafting of molecular complexes on support usually leads to a drastic loss of activity compared to that of the homogeneous equivalent.[4]

Having this MOF-supported nickel complexes in hand, we explore their potential as heterogeneous catalysts for this reaction in the liquid phase. Typically, Ni@(Fe)MIL-101 suspended in heptane is allowed to react in the presence of Et$_2$AlCl under 15 bar of ethylene. After quenching, the products are analyzed by gas chromatography to determine the catalytic activity defined as moles of oligomers formed per mole of nickel per hour. Results obtained with our solids as well as with analogous molecular species under these "early" conditions are summarized in the Table 1.

Table 1. Ni-Catalyzed Ethylene Oligomerization in Liquid Phase under "Early" Conditions^a

entry	catalyst (μmol)^b	intrinsic activity (h^{-1})^c	selectivity (%)^c		
			C$_4$	C$_6$	C$_8$
1	none	0	0	0	0
2	Ni(PPh$_3$)$_2$Cl$_2$ (35)	9540	84	15.6	0.4
3	Ni(bipy)Cl$_2$ (35)	175	92	8	0
4	Ni(bipy)Cl$_2$ (2.8)	210	92	7.5	0.5
5	(Fe)MIL-101-NH$_2$^{d}	0	0	0	0
6	(Fe)MIL-101-NH$_2$ + NiCl$_2$^{e}	0	0	0	0
7	(Fe)MIL-101-NH$_2$ + PyCHO^f	0	0	0	0
8	30Ni@(Fe)MIL-101 (8.4)	3215	94	5.5	0.5
9	10Ni@(Fe)MIL-101 (2.8)	3166	95	4.5	0.5

^{a}Reaction performed in n-heptane in the presence of Et$_2$AlCl (Al/Ni = 70) under 15 bar of ethylene at 10 °C. ^{b}Based on the amount of Ni, corresponding to 8 mg of Ni@(Fe)MIL-101. ^{c}Estimated by GC analysis and calculated as moles of oligomer formed/(moles of Ni·h). ^{d}Reaction performed using 8 mg of MOF. ^{e}Reaction performed using 8 mg of MOF and NiCl$_2$ (35 μmol, 4.5 mg). ^{f}Reaction performed using 8 mg of MOF and PyCHO (10 μmol, 1 μL), the activity is here calculated as moles of oligomer formed/(moles of PyCHO·h).

As expected, the reaction does not proceed in the presence of the (Fe)MIL-101-NH$_2$ alone or combined with either NiCl$_2$ or PyCHO (entries 1 and 5−7). Even if bis(triphenylphosphine) nickel dichloride complex shows the highest activity (entry 2), the Ni@(Fe)MIL-101 catalyst remains more than 10 times more active than its molecular analogue Ni(bipy)Cl$_2$ (entries 3 and 4). With turnover frequencies up to 3215 h^{-1} at 10 °C, the catalytic activity found with Ni-functionalized (Fe)MIL-101 is higher than those found for coordination polymer catalysts reported by Angelescu[16] and Miyake[17] in the literature (Table S2).

Moreover, the similar activity obtained using 10Ni- and 30Ni@(Fe)MIL-101 tends to demonstrate that all the catalytic sites are accessible (entries 8 and 9).

It is noteworthy that here almost only 1-butene is formed during the reaction (>95%, Supporting Information). Using nickel pyridinimino complex anchored into (Fe)MIL-101,

higher 1-butene selectivity is found than those commonly reported with molecular bis- or tridentate imino nickel species ($\leq$80%),[18] the data remaining however difficult to compare due to differences in reaction conditions.

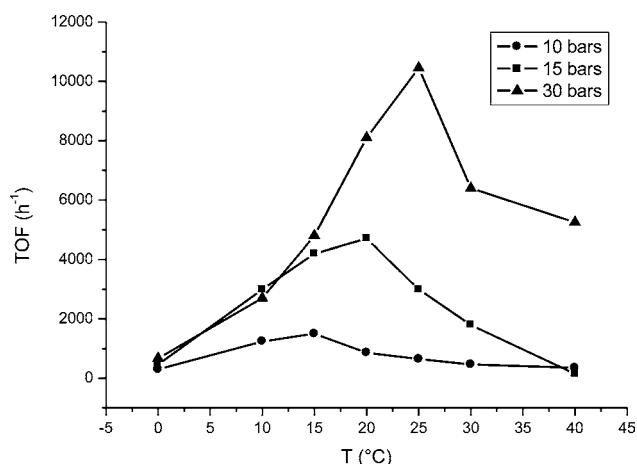The temperature-dependence of the catalytic activity of 10Ni@(Fe)MIL-101 is highlighted in Figure 1. The catalytic

Figure 1. Temperature-dependent activity of 10Ni@(Fe)MIL-101 in the liquid phase ethylene oligomerization.

activity reaches a maximum which is displaced to higher temperatures when the pressure increases. At 30 bar and 25 °C, the highest activity is 10 455 mol of oligomers formed/(mol Ni·h), which corresponds to 205 g of butene/(g of MOF material·h). A similar temperature-dependence can be found in literature in the case of homogeneous[18b,d] as well as covalently supported nickel diimine molecular catalysts.[19] Moreover, the activity obtained using 10Ni@(Fe)MIL-101 catalyst under optimized conditions is in the range of those reported for supported nickel complexes coordinated either by phosphines[20] or by sophisticated Schiff bases (Table S2).[19,21]

Leaching test shows that the reaction does not proceed any longer if the filtrated catalytic solution is again put under catalytic conditions in the presence of Al-based co-catalyst. PXRD analysis of 10Ni@(Fe)MIL-101 after a catalytic run confirms that its crystallinity is preserved. Furthermore, the 10Ni@(Fe)MIL-101 can be reused, after careful washings with anhydrous ethanol and drying, for at least two more catalytic runs without significant loss of activity or selectivity (Supporting Information).

In conclusion, we have developed a novel one-pot postfunctionalization of a metal organic framework enabling the immobilization of an active organometallic catalyst in its cavities. This new MOF catalyst is very efficient in the triphasic ethylene dimerization producing selectively 1-butene. The single-site isolation combined with high site density onto the MOF leads to high activity. Furthermore, higher selectivity for 1-butene is found using the Ni@(Fe)MIL-101 catalyst than reported for molecular nickel diimino complexes. Thus, this original catalytic porous material, made from relatively cheap precursors, opens new perspectives for the use of MOF-based catalysts in valorization processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Full synthetic details, compounds characterizations (PXRD, SEM-EDX, NMR, adsorption isotherms) and catalysis. This

material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
jerome.canivet@ircelyon.univ-lyon1.fr
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Candy, J. P.; Didillon, B.; Smith, E. L.; Shay, T. B.; Basset, J. M. *J. Mol. Catal.* **1994**, *86*, 179. (b) Coperet, C.; Chabanas, M.; Saint-Arroman, R. P.; Basset, J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 156. (c) Vidal, V.; Theolier, A.; ThivolleCazat, J.; Basset, J. M. *Science* **1997**, *276*, 99.
(2) (a) Corriu, R. J. P.; Mehdi, A.; Reye, C.; Thieuleux, C.; Frenkel, A.; Gibaud, A. *New J. Chem.* **2004**, *28*, 156. (b) Joubert, J.; Delbecq, F.; Sautet, P.; Le Roux, E.; Taoufik, M.; Thieuleux, C.; Blanc, F.; Coperet, C.; Thivolle-Cazat, J.; Basset, J.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9157.
(3) (a) Pugin, B. *J. Mol. Catal., A: Chem.* **1996**, *107*, 273. (b) Zhang, T.; Song, F.; Lin, W. *Chem. Commun.* **2012**, *48*, 8766.
(4) (a) Collins, S.; Kelly, W. M.; Holden, D. A. *Macromolecules* **1992**, *25*, 1780. (b) Kristen, M. O. *Top. Catal.* **1999**, *7*, 89.
(5) (a) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450. (b) Xamena, F.; Abad, A.; Corma, A.; Garcia, H. *J. Catal.* **2007**, *250*, 294. (c) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Edit.* **2009**, *48*, 7502. (d) Corma, A.; Garcia, H.; Xamena, F. X. L. *Chem. Rev.* **2010**, *110*, 4606.
(6) (a) Vansant, E. F.; Van der Voort, P.; Vrancken, K. C. In *Characterization and Chemical Modification of the Silica Surface*; Elsevier: New York, 1995; Vol. 93, p 149. (b) Zhuravlev, L. T. *Langmuir* **1987**, *3*, 316. (c) Coasne, B.; Galarneau, A.; Di Renzo, F.; Pellenq, R. J. M. *Langmuir* **2006**, *22*, 11097.
(7) (a) Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, *309*, 2040. (b) Wang, B.; Cote, A. P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2008**, *453*, 207. (c) Hong, D.-Y.; Hwang, Y. K.; Serre, C.; Ferey, G.; Chang, J.-S. *Adv. Funct. Mater.* **2009**, *19*, 1537.
(8) (a) Cohen, S. M. *Chem. Sci.* **2010**, *1*, 32. (b) Wang, Z. Q.; Cohen, S. M. *Chem. Soc. Rev.* **2009**, *38*, 1315. (c) Cohen, S. M. *Chem. Rev.* **2012**, *112*, 970.
(9) (a) Bhattacharjee, S.; Yang, D.-A.; Ahn, W.-S. *Chem. Commun.* **2011**, *47*, 3637. (b) Bloch, E. D.; Britt, D.; Lee, C.; Doonan, C. J.; Uribe-Romo, F. J.; Furukawa, H.; Long, J. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2010**, *132*, 14382. (c) Chavan, S.; Vitillo, J. G.; Uddin, M. J.; Bonino, F.; Lamberti, C.; Groppo, E.; Lillerud, K.-P.; Bordiga, S. *Chem. Mater.* **2010**, *22*, 4602. (d) Doonan, C. J.; Morris, W.; Furukawa, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 9492. (e) Ingleson, M. J.; Barrio, J. P.; Guilbaud, J. B.; Khimyak, Y. Z.; Rosseinsky, M. J. *Chem. Commun.* **2008**, 2680. (f) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 806. (g) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. *Nat. Chem.* **2010**, *2*, 838. (h) Tanabe, K. K.; Cohen, S. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7424. (i) Wang, C.; Xie, Z.; deKrafft, K. E.; Lin, W. *J. Am. Chem. Soc.* **2011**, *133*, 13445. (j) Zhang, X.; Llabres, F.; Corma, A. *J. Catal.* **2009**, *265*, 155.

(10) Banerjee, M.; Das, S.; Yoon, M.; Choi, H. J.; Hyun, M. H.; Park, S. M.; Seo, G.; Kim, K. *J. Am. Chem. Soc.* **2009**, *131*, 7524.

(11) Hwang, Y. K.; Hong, D.-Y.; Chang, J.-S.; Jhung, S. H.; Seo, Y.-K.; Kim, J.; Vimont, A.; Daturi, M.; Serre, C.; Ferey, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 4144.

(12) (a) Esken, D.; Zhang, X.; Lebedev, O. I.; Schroder, F.; Fischer, R. A. *J. Mater. Chem.* **2009**, *19*, 1314. (b) Meilikhov, M.; Yusenko, K.; Esken, D.; Turner, S.; Van Tendeloo, G.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2010**, 3701. (c) Huang, Y. B.; Lin, Z. J.; Cao, R. *Chem.—Eur. J.* **2011**, *17*, 12706. (d) Muller, M.; Turner, S.; Lebedev, O. I.; Wang, Y. M.; van Tendeloo, G.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2011**, 1876.

(13) Latroche, M.; Surble, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J.-H.; Chang, J.-S.; Jhung, S. H.; Ferey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8227.

(14) (a) Bauer, S.; Serre, C.; Devic, T.; Horcajada, P.; Marrot, J.; Ferey, G.; Stock, N. *Inorg. Chem.* **2008**, *47*, 7568. (b) Hartmann, M.; Fischer, M. *Microporous Mesoporous Mater.* **2012**, *164*, 38.

(15) (a) AlSherehy, F. A. *Stud. Surf. Sci. Catal.* **1996**, *100*, 515. (b) Cauvin, S.; Braunschweig, B.; Galtier, P.; Glaize, Y. *Rev. Inst. Fr. Pet.* **1992**, *47*, 375. (c) Freitas, E. R.; Gum, C. R. *Chem. Eng. Prog.* **1979**, *75*, 73. (d) Keim, W. *Chem. Ing. Tech.* **1984**, *56*, 850. (e) Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21. (f) Lutz, E. F. *J. Chem. Educ.* **1986**, *63*, 202. (g) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594. (h) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

(16) Angelescu, E.; Che, M.; Andruh, M.; Zavoianu, R.; Costentin, G.; Mirica, C.; Pavel, O. D. *J. Mol. Catal., A: Chem.* **2004**, *219*, 13.

(17) Kyogoku, K.; Yamada, C.; Suzuki, Y.; Nishiyama, S.; Fukumoto, K.; Yamamoto, H.; Indo, S.; Sano, M.; Miyake, T. *J. Jpn. Pet. Inst.* **2010**, *53*, 308.

(18) (a) de Souza, R. F.; Bernardo-Gusmao, K.; Cunha, G. A.; Loup, C.; Leca, F.; Reau, R. *J. Catal.* **2004**, *226*, 235. (b) Liu, F.-S.; Gao, H.-Y.; Song, K.-M.; Zhang, L.; Zhu, F.-M.; Wu, Q. *Polyhedron* **2009**, *28*, 1386. (c) Smetanyuk, V. I.; Ivanyuk, A. V.; Martynova, M. A.; Komarova, O. P. *Pet. Chem.* **2003**, *43*, 28. (d) Wang, K.; Gao, R.; Hao, X.; Sun, W.-H. *Catal. Commun.* **2009**, *10*, 1730. (e) Lecocq, V.; Olivier-Bourbigou, H. *Oil Gas Sci. Technol.* **2007**, *62*, 761.

(19) (a) AlObaidi, F.; Ye, Z. B.; Zhu, S. P. *Macromol. Chem. Phys.* **2003**, *204*, 1653. (b) Li, Y.-G.; Pan, L.; Zheng, Z.-J.; Li, Y.-S. *J. Mol. Catal., A: Chem.* **2008**, *287*, 57. (c) Schrekker, H. S.; Kotov, V.; Preishuber-Pflugl, P.; White, P.; Brookhart, M. *Macromolecules* **2006**, *39*, 6341. (d) Preishuber-Pflugl, P.; Brookhart, M. *Macromolecules* **2002**, *35*, 6074.

(20) Braca, G.; Galletti, A. M. R.; Digirolamo, M.; Sbrana, G.; Silla, R.; Ferrarini, P. *J. Mol. Catal., A: Chem.* **1995**, *96*, 203.

(21) (a) Song, K.-M.; Gao, H.-Y.; Liu, F.-S.; Pan, J.; Guo, L.-H.; Zai, S.-B.; Wu, Q. *Catal. Lett.* **2009**, *131*, 566. (b) Choi, Y.; Soares, J. B. P. *Macromol. Chem. Phys.* **2009**, *210*, 1979.