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Communication

Friedel-Crafts Alkylation of Toluene as a Parallel Reaction in Propylene Dimerization Catalyzed by Nickel β-Diimine Complex/EASC in Homogeneous Phase

***Isabel Vicente, Katia Bernardo-Gusmão, Michèle O. de Souza* and Roberto F. de Souza*†**

Laboratório de Reatividade e Catálise, Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre-RS, Brazil

A oligomerização do propeno foi realizada utilizando o complexo dibromo-bis(*N*,*N'*-difenilpentano-2,4-diimina)niquel(II) como precursor catalítico combinado ao sesquicloreto de etilalumínio ($Al_2Et_3Cl_3$, EASC) como co-catalisador. A 10 ºC, usando o tolueno como solvente, altas frequências de rotação foram obtidas (até 57000 h^{-1}) com alta seletividade em produtos C_6 (até > 99%) e seletividade moderada em C_6 linear (até 29%). Observou-se que nas condições experimentais empregadas o propeno reagiu com tolueno por reação de Friedel-Crafts. O aumento da concentração de precursor catalítico, mantendo constante a relação precursor/co-catalisador, teve por efeito de aumentar a selectividade para os produtos de oligomerização em relação aos produtos de alquilação por reação de Friedel-Crafts.

Propylene oligomerization was performed using dibromo-bis(*N,N'*-diphenylpentane-2,4-diimine)nickel(II) complex as catalytic precursor combined with ethyl aluminum sesquichloride ($Al_2Et_3Cl_3$, EASC) as co-catalyst. At 10 ºC, using toluene as solvent, high turnover frequencies (up to 57,000 h^{-1}) with high selectivities to C_6 products (up to > 99%) and moderate linear C_6 selectivity (up to 29%) were obtained. Under our reaction conditions propylene reacted with toluene through Friedel-Crafts reaction. Increasing the concentration of catalyst precursor keeping the nickel complex/co-catalyst ratio constant increased the selectivity of the oligomerization products *vs.* Friedel-Craft products.

Keywords: nickel, ß-diimine ligands, propylene oligomerization, Friedel-Crafts alkylation

Introduction

The oligomerization of ethylene and propylene is commonly used to obtain short-chain alkenes in industrial processes. Among the resulting olefins, linear α-olefins are extensively employed as building blocks for the synthesis of a variety of products, such as polymers, detergents and plasticizers.[1] The choice of the catalyst involves not only the selectivity to α-olefin formation, but also the requirement of the linear products, whose formation depends on the regioselectivity of the carbon-carbon bond formation reactions.[2] There is a plethora of transition metal catalysts that are active for these processes.[3,4] Among them, nickel(II) catalytic precursors containing α- and β-diimine ligands (Figure 1) display high efficiency for the ethylene oligomerization reaction.[5,6]

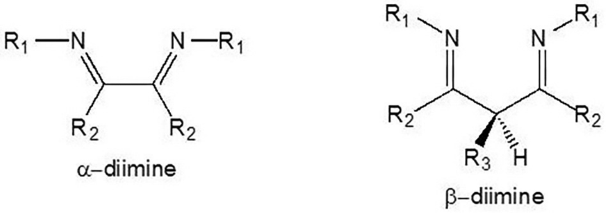

Figure 1. General structure of α-diimines and ß-diimines.

The use of α-diimine and β-diimine ligands is highly advantageous since their synthesis can be achieved by simple reaction between the desired diketone and the corresponding amine, thus allowing the study of the steric effect of the ligand and the electronic properties on the catalytic performance.[6] Moreover, ß-diimine ligands have higher stability to decomposition than phosphorus(III)-based compounds, which have extensively been used as ligands of the catalytic precursors for these processes.[1]

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*e-mail: michele.souza@ufrgs.br

†*In memoriam*

In most cases, oligomerization of olefins involving nickel complexes is attributed to the reaction of metal-hydride species, usually generated by the reaction of a co-catalyst with a transition metal complex (catalytic precursor).[7] Among these co-catalysts, the most commonly employed are alkylaluminum compounds, which have been intensively studied.[8-10] Among them, ethyl aluminum sesquichloride ($Al_2Et_3Cl_3$, EASC) is demonstrated to be advantageous because of its low cost and also because it increases the selectivity towards oligomerization products *vs.* polymerization products.[10]

It has recently been reported that alkylaluminum species could favor the formation of toluene (PhMe) alkylation products.[11] Under oligomerization reaction conditions, this process could operate as a side-reaction since aromatic compounds are commonly used as solvents. Herein, the application of dibromobis(*N,N'*-diphenylpentane-2,4-diimine)nickel(II) complex (**C**), as catalytic precursor for the propylene oligomerization reaction using EASC as co-catalyst is reported. The influence of the concentration of catalytic precursor maintaining the nickel complex/co-catalyst ratio constant on the catalytic performance (activity and selectivity) was studied.

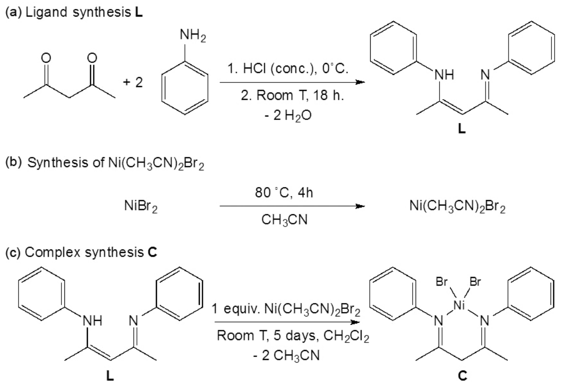
Experimental

General methods

All syntheses were performed under argon, using Schlenk tube techniques. Solvents (Tedia) were purified by standard procedures.[12] Ethylaluminum sesquichloride ($Al_2Et_3Cl_3$, EASC) was supplied by Akzo Nobel and used with previous dilution with toluene (10%). All other reagents (Sigma) were used as received. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with an Agilent 400 MHz spectrometer. Chemical shifts are relative to $CDCl_3$ (^1H and ^{13}C). Infrared (IR) spectra were recorded on a Shimadzu IR Prestige-21 spectrometer. The spectra were acquired by accumulating 32 scans at 4 cm^{-1} resolution in the range of 400-4000 cm^{-1}. CHN analyses of the samples were obtained with a CHN Perkin Elmer M CHN 2400 analyser.

Catalytic precursor synthesis

Scheme 1 shows the synthesis of 2-(phenyl)amino-4-(phenyl)imino-2-pentene (**L**), $Ni(MeCN)_2Br_2$ and dibromobis(*N,N'*-diphenylpentane-2,4-diimine)nickel(II) complex (**C**).



Scheme 1. Synthesis of: (a) 2-(phenyl)amino-4-(phenyl)imino-2-penteno (**L**), (b) $Ni(MeCN)_2Br_2$, (c) dibromobis(*N,N'*-diphenylpentane-2,4-diimine)nickel(II) complex (**C**).

The ligand 4-(phenylamino)-2-(phenylimino)-3-pentene (**L**) was synthesized following a reported procedure.[6] A solution of acetylacetone (10.4 mL, 100 mmol) and aniline (18.5 mL, 200 mmol), was cooled down to 0 ºC and 8.3 mL of hydrochloric acid was slowly added under stirring. The mixture was stirred for 18 h at room temperature and subsequently filtered. The obtained solid was dissolved in 60 mL of CH_2Cl_2. To the resulting solution 80 mL of Na_2CO_3 saturated aqueous solution was added. The aqueous phase was separated from the organic phase and extracted with two 20 mL aliquots of CH_2Cl_2. The organic phases were collected and the solvent was evaporated under vacuum. The crude product was recrystallized with methanol obtaining 10.26 g of **L** (41.0 mmol, 41% yield, Scheme 1a) and charactarized by IR spectroscopy (C=N deformation in 1634 cm^{-1}), ^1H NMR (400.0 MHz, $CDCl_3$) and ^{13}C NMR (100.6 MHz, $CDCl_3$) (see spectra in Figures S1 and S2, respectively, and the corresponding spectroscopic data in the Supplementary Information).

$Ni(MeCN)_2Br_2$ was synthesized according to Hathaway and Holah synthesis.[13] A mixture of $NiBr_2$ (5.845 g, 26.2 mmol) and 240 mL acetonitrile (MeCN) was refluxed for 4 h at 80 ºC. The mixture was filtered and the resulting solid was dried under Ar flow (1 mL s^{-1}), obtaining 5.03 g of product (88% yield, Scheme 1b). Experimental CHN: C 15.7%, H 2.2%, N 9.1%; theoretical: C 16.0%, H 2.0%, N 9.3%.

Complex **C** was synthesized following a previously reported procedure.[6] A solution of 4-(phenylamino)-2-(phenylimino)-3-pentene (**L**, 1.502 g, 6 mmol) in 20 mL CH_2Cl_2 was added to a suspension of $Ni(MeCN)_2Br_2$ (1.80 g, 6 mmol) and 40 mL CH_2Cl_2 and then stirred for 5 days at room temperature. The mixture was filtered and the solvent was removed under vacuum obtaining 0.630 g of **C** (1.3 mmol, 22% yield, Scheme 1c). Experimental CHN: C 42.8%; H 4.5%; N 5.6%; theoretical: C 43.5%, H 3.7%, N 6.0%; IR ν_{max}/cm^{-1} 1674 (C=N).

Catalytic tests

Propylene oligomerization tests were performed using a 450 mL stainless steel Parr reactor with magnetic drive mechanical stirring. Typical catalytic run conditions were: 30 min, 10 ± 2 ºC (reaction temperature controlled with a thermostatic circulation bath), 60 mL of solvent, 20 µmol of **C**, EASC in a ratio Al:Ni of 100:1, and propylene pressure of 6 bar maintained constant during the experiment. HCl-acidified ethanol (2% HCl m/m) was added to the reaction mixture and an aliquot of 1 mL of the reaction mixture was taken. To this aliquot, aproximately 50 mg of isooctane was added and the sample was analysed by gas chromatography (GC).

Gas chromatography coupled to a flame ionization detector (GC-FID) and gas chromatography-mass spectrometry (GC-MS) analyses of the reaction mixtures were performed in order to determine the nature and amount of products. GC-FID analysis were carried out with a Shimadzu GC-2010 gas chromatograph equipped with a 100 m long Petrocol DH capillary column coated with methylsilane and using isooctane as internal standard. GC-MS were carried out with a Shimadzu GC-2010 gas chromatograph equipped with a 100 m long Petrocol DH capillary column coated with methylsilane. ^{1}H NMR experiments of the mono-, di- and tri-alkylated products fractions were performed with an Agilent 400 MHz spectrometer.

Results and Discussion

Table 1 displays results of propylene oligomerization performed with **C** complex as catalytic precursor, and EASC as co-catalyst using PhMe as solvent (Table 1, entries 1-6). For comparison a blank test without the catalytic precursor (**C**) has been performed (Table 1, entry 7). All experiments were conducted with a constant solvent volume of 60 mL.

Catalytic activity is displayed in terms of turnover frequency (TOF, mol of propylene consumed × mol Ni^{-1} × h^{-1}). Since propylene oligomerization and alkylation of toluene with propylene were observed (Figure 2), selectivity is displayed in terms of the amount of propylene incorporation to each fraction.

In order to address the structure of alkylation products, NMR (Figures 3 and S3) and GC-MS analysis (Figure S4) were carried out and revealed the formation of mono-(C_{10}), di-(C_{13}) and tri-(C_{16}) alkylation products of PhMe with propylene inserted through the C2-carbon.

The active catalytic species for propylene oligomerization is the nickel hydride Ni(II)–H formed by alkylation reaction of the nickel catalytic precursor **C** with the co-catalyst EASC.[7,14] For better comparison of propylene dimerization results, the parameters p and q, previously defined by Bogdanović,[2,14] have been calculated. The dimerization of propylene can be described as a sequence in which propylene is inserted into a Ni(II)–H bond followed by insertion of a second molecule of propylene, forming the Ni(II)–C_3H_7 species (Scheme 2).

Table 1. Propylene conversion using **C** as catalytic precursor and EASC as co-catalyst[a]

entry	n_{Ni} / µmol	n_{Al} / µmol	TOF_{olig}[b] / (10^3 h^{-1})	TOF_{alk}[c] / h^{-1}	%Propylene converted for the synthesis of:					Oligomerization selectivity[f] / %			p_g C1/C2	q_g C1/C2
					C_6[d]	C_9[d]	C_{10}[e]	C_{13}[e]	C_{16}[e]	DMB	MP	n-H		
1	40	4000	38	–	> 99	–	–	–	–	10	61	29	29/71	10/90
2	20	2000	57	10	97	2	–	–	1	0	75	25	25/75	5/95
3	15	1500	31	40	88	–	4	2	6	7	65	28	28/72	7/93
4	10	1000	13	40	78	–	9	4	9	6	67	27	28/72	7/93
5	5	500	10	40	69	–	10	6	15	6	66	28	28/72	6/94
6	5	2000	49	< 10	98	–	1	0	1	8	65	27	27/73	8/92
7	0	2000	–	320	–	–	24	19	57	–	–	–	–	–

[a]General reaction conditons: co-catalyst = EASC, $P_{propylene}$ = 6 bar, solvent: toluene 60 mL, t = 30 min, T = 10 ºC; [b]oligomerization turnover frequency (TOF): mol of propylene consumed × mol Ni^{-1} × h^{-1}; [c]alkylation TOF: mol of propylene consumed × mol Al^{-1} × h^{-1}; [d]oligomerization products; [e]toluene mono-(C_{10}), di-(C_{13}) and tri-alkylation (C_{16}) products; [f]DMB: dimethylbutenes; MP: methylpentenes; n-H: linear hexenes. p_g: propylene insertion proportion (C1-insertion/C2-insertion) of the first insertion. q_g: propylene insertion proportion (C1-insertion/C2-insertion) of the second insertion.

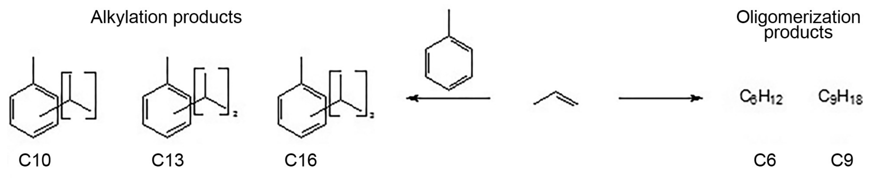


Figure 2. PhMe alkylation products with propylene (left) and propylene oligomerization products (right).

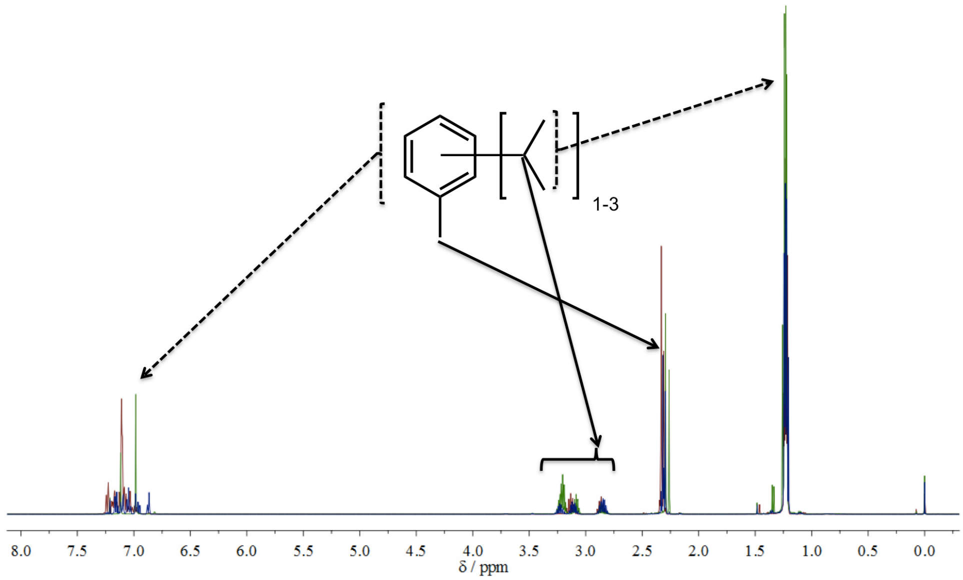
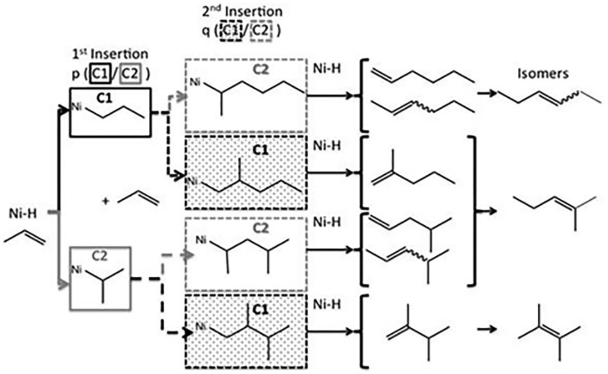


Figure 3. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of the mono-, di- and tri-alkylated product fractions.

A further β-elimination step allows the formation of the C_6-isomers together with the regeneration of the active Ni(II)–H catalytic species. As propylene is a dissymmetric molecule, its insertion into the nickel species can occur through its carbon 1 (Ni → C1) or its carbon 2 (Ni → C2). Thus, each C_6-isomer can be described as a specific insertion sequence of propylene. Using propylene dimer selectivity, the parameters p and q enable to quantify the propylene insertion proportion (C1-insertion/C2-insertion) of the first and second insertion, respectively (Scheme 2).



Scheme 2. Illustration of the insertion mode of propylene (through the C1 or C2 carbon), during propylene dimerization catalyzed by the Ni(II)–H species.

The blank test (Table 1, entry 7) showed that the use of EASC lead exclusively to the formation of alkylation products. As long as the nickel complex was combined with an excess of EASC in the presence of propylene (Table 1, entries 1-6), oligomerization took place with a much higher activity than that of alkylation.

Figures 4 and 5 display respectively: (*i*) the oligomerization TOF and alkylation TOF (Table 1, entries 1-5) and; (*ii*) the alkylation products (mono-, di- and trialkylation of toluene) selectivities among all products (Table 1, entries 2-5) as a function of the amount of EASC maintaining the Al/Ni ratio equal to 100.

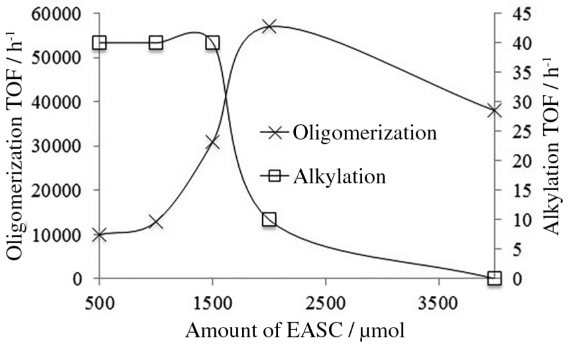


Figure 4. Oligomerization TOF and alkylation TOF using **C** as catalytic precursor as a function of the EASC amounts at constant Al/Ni = 100.

Results of catalytic reaction conducted varying the Ni(II)-catalytic precursor **C** and EASC amounts, maintaining constant the aluminum to **C** ratio equal to 100 and the solvent volume (60 mL of toluene) (Table 1, entries 1-5) show that the increase of EASC amount produced an increase in the oligomerization activity (Figure 4). This behavior could be ascribed to the presence of higher concentration of Ni catalytically-active species when higher catalytic precursor and co-catalysts amounts were employed, thus corresponding to higher oligomerization rates *vs.* alkylation rates. Comparison of entries 5 and 6, corresponding to experiments conducted

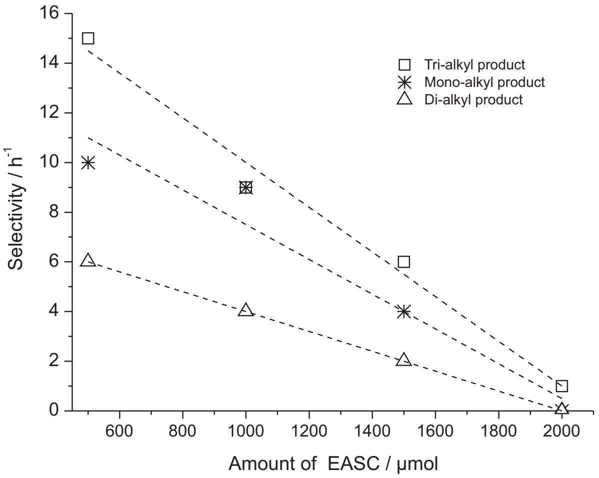


Figure 5. Selectivity to alkylation products (mono-, di- and tri-alkylation of toluene) among all products using **C** as catalytic precursor as a function of EASC.

with a lower amount of nickel (5 mmol), showed that augmenting the amount of EASC (Al/Ni = 100 to 400) lead to an increase of oligomerization activity, indicating again that more active nickel species were generated when employing a great EASC excess.

Oligomerization selectivities showed that no significant changes in *n*-hexene selectivity (i.e., 25-29%) were observed when oligomerization activity was modified. As far as alkylation selectivity is concerned, similar linear decrease for all alkyl products were observed (Figure 4) when alkylation activity decreased, indicating that the proportion between the mono-, di- and tri-alkyl products remained constant. These selectivity results might indicate that the activities of the catalytic species are modified due to the change in their concentration but the nature of the catalytic species is not altered. The same conclusion can be drawn for the dimerization as p and q values remain similar (Table 1, entries 1-6).

Hence, the alteration of oligomerization activities observed by varying the Ni(II)-catalytic precursor **C** and EASC concentrations indicated that the amount of active species for oligomerization depended on the catalytic precursor and co-catalysts' concentration. The increase of oligomerization activity observed when Ni(II)-catalytic precursor C and EASC concentration are incresead might be explained by the formation of more nickel active species in the presence of higher concentrations of the co-catalyst. The more the co-catalyst concentration was increased the higher the oligomerization species concentration and the higher the oligomerization rate *vs.* alkylation rate. Forty mmol of nickel precursor and co-catalyst (Table 1, entry 1), representing the highest concentration herein tested, lead to almost exclusively oligomerization products. This result illustrated the competitive effect between the oligomerization and alkylation reactions. Previous studies described the influence of alkyl co-catalyst concentration in the activation of Ziegler-Natta systems, reporting that different alkyl aggregates were formed as a function of its concentration, which affected the efficiency for metal-catalytic precursor activation reactions.[15]

As for the blank test is concerned (Table 1, entry 5) it revealed that EASC catalyzed the toluene alkylation, amounting to a TOF of 320 h^{-1}. This activity value was about 10 times higher than the value obtained when the nickel system was present in the reaction medium (Table 1, entries 2 and 6). This behavior should be ascribed to the consumption of the alkylating agent during the activation of the Ni-catalytic precursors. Thus, alkylation of toluene with propylene can be considered as a side reaction that occurs during propylene oligomerization due to the presence of the co-catalyst. This hypothesis is corroborated by the fact that when the oligomerization activity increased, the alkylation activity decreased (see Figure 4). Recent reports described the formation of toluene alkylation products by the *in situ* reaction of toluene with the oligomers formed during ethylene oligomerization using Ni(II)-complexes as catalytic precursors and alkyl aluminum reagents as co-catalyst.[11] The authors suggested that the produced oligomers were much more reactive for the alkylation process than ethylene. In the present case propylene is much more reactive for the Friedel-Crafts alkylation reaction than the produced dimers.

Conclusions

In conclusion, results are reported for the propylene oligomerization performed using dibromo-bis(*N,N'*-diphenylpentane-2,4-diimine)nickel(II) as catalytic precursor combined with ethyl aluminum sesquichloride ($Al_2Et_3Cl_3$, EASC) as co-catalyst. At 10 ºC, using toluene as solvent, high turnover frequencies (up to 57,000 h^{-1}) with high selectivities to the C_6 products (up to > 99%) and moderate linear C_6 selectivity (up to 29%) were achieved. It is to noteworthy that under our reaction conditions propylene reacted with toluene through a Friedel-Crafts reaction and that alkylation products were formed in higher amounts when nickel species concentration is the lowest. Increasing the nickel complex concentration maintaining the Al/Ni ratio equal to 100, the oligomerization activity *vs.* alkylation activity increased and oligomerization selectivity remained unchanged. Selectivity results showed that this behavior can be ascribed to the higher concentration of Ni catalytically-active species when higher catalytic precursor and co-catalysts amounts were employed, maintaining their ratio constant and thus higher oligomerization rates *vs.* alkylation rates were observed. Therefore, we have demonstrated that the Friedel-Crafts alkylation of toluene (the common solvent used in oligomerization laboratory tests) with alkenes under oligomerization conditions should be taken in consideration as a side-process, especially when reactions are performed at low metal precursor and alkylation co-catalyst concentrations.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgements

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This work is dedicated to Prof Roberto Fernando de Souza, who left us prematurely. It was a great privilege to work with him, a very special person and gifted scientist. He leaves an immense scientific legacy and will be missed by all who had the pleasure to know him.

References

1. van Leeuwen, P. W. N. M.; *Homogeneous Catalysis: Understanding the Art*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2004.
2. de Souza, M. O.; de Souza, R. F.; Rodrigues, L. R.; Pastore, H. O.; Gauvin, R. M.; Gallo, J. M. R.; Favero, C.; *Catal. Commun.* **2013**, *32*, 32.
3. Wang, S.; Sun, W.-H.; Redshaw, C.; *J. Organomet. Chem.* **2014**, 751, 717.
4. Chirila, A.; Wolf, R.; Slootweg, J. C.; Lammertsma, K.; *Coord. Chem. Rev.* **2014**, *57*, 270; Boudier, A.; Breuil, P.-A.; Magna, L.; Olivier-Bourbigou, H.; Braunstein, P.; *Chem. Commun.* **2014**, *50*, 1398; Fujita, T.; Kawai, K.; *Top Catal.* **2014**, *57*, 852; Ma, J.; Feng, C.; Wang, S.; Zhao, K.-Q.; Sun, W.-H; Redshaw, C.; Sloan, G. A.; *Inorg. Chem. Front.* **2014**, *1*, 14; Wang, S.; Sun, W.-H.; Redshaw, C.; *Dalton Trans.* **2013**, *42*, 8988; Keim, W.; *Angew. Chem., Int. Ed.* **2013**, *52*, 12492; Bryliakov, K. P.; Talsi, E. P.; *Coord. Chem. Rev.* **2012**, *256*, 2994; Giambastiani, G.; Luconi, L.; Kuhlman, R. L.; Hustard, P. D. In *Olefin Upgrading Catalysis by Nitrogen-based Metal Complexes I, Catalysis by Metal Complexes*, vol. 35; Campora, J.; Giambastiani, G., eds.; Springer: Dordrecht, 2011, ch. 5; McGuiness, D. S.; *Chem. Rev.* **2011**, *111*, 2321; Agapie, T.; *Coord. Chem. Rev.* **2011**, *255*, 861.
5. Killian, C. M.; Johnson, L. K.; Brookhart, M.; *Organometallics* **1997**, *16*, 2005; Johnson, L. K.; Killian, C. M.; Brookhart, M.; *J. Am. Chem. Soc.* **1995**, *117*, 6414.
6. Rosetto, E.; Caovilla, M.; Thiele, D.; de Souza, R. F.; Bernardo-Gusmao, K.; *Appl. Catal., A* **2013**, *454*, 152; Wyrvalski, C. N.; de Souza, M. O.; de Souza, R. F.; *Quim. Nova*, **1996**, *19*, 493; Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D.; *Organometallics* **1997**, *16*, 1514.
7. Thiele, D.; de Souza, R. F.; *Catal. Lett.* **2010**, *138*, 50.
8. Tayade, K. N.; Mane, M. V.; Sen, S.; Murthy, C. N.; Tembe, G. L.; Pillai, S. M.; Vanka, K.; Mukherjee, S.; *J. Mol. Catal. A: Chem.* **2013**, *366*, 238; Maldanis, R. J.; Wood, J. S.; Chandrasekaran, A.; Rausch, M. D.; Chien, J. C. W.; *J. Organomet. Chem.* **2002**, *645*, 158.
9. Wyrvalski, C. N.; de Souza, M. O.; de Souza, R. F.; *Quim. Nova* **1996**, *5*, 19; Eberhard, G. G.; Griffin, W. P.; *J. Catal.* **1970**, *16*, 245.
10. de Souza, C. G.; de Souza, R. F.; Bernardo-Gusmão, K.; *Appl. Catal., A* **2007**, *325*, 87.
11. Budhai, A.; Omondi, B.; Ojwach, S. O.; Obuah, C.; Osei-Twum, E. Y.; Darkwa, J.; *Catal. Sci. Technol.* **2013**, *3*, 3130; Ojwach, S. O.; Guzei, I. A.; Benade, L. L.; Mapolie, S. F.; Darkwa, J.; *Organometallics* **2009**, *28*, 2127; Song, K.; Gao, H.; Liu, F.; Pan, J.; Guo, L.; Zai, S.; Wu, Q.; *Eur. J. Inorg. Chem.* **2009**, 3016; Dyer, P. W.; Fawcett, J. M.; Hanton, J.; *Organometallics* **2008**, *27*, 5082.
12. Armarego, W. L. F.; Perrin, D. D.; *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heineman: Oxford, UK, 1997.
13. Hathaway, B. J.; Holah, D. G.; *J. Chem. Soc.* **1964**, 2400.
14. Bogdanovic, B.; *Adv. Organomet. Chem.* **1979**, *17*, 105.
15. Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F.; *Chem. Rev*. **2000**, *100*, 1253; Jüngling, S.; Mülhaupt, R.; *J. Organomet. Chem.* **1995**, *497*, 27.

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