



Covalent organic frameworks as supports for a molecular Ni based ethylene oligomerization catalyst for the synthesis of long chain olefins



Elena Rozhko, Anastasiya Bavykina, Dmitrii Osadchii, Michiel Makkee, Jorge Gascon*

Delft University of Technology, Chemical Engineering Department, Catalysis Engineering, Van der Maasweg 9, 2629 HZ Delft, The Netherlands

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ABSTRACT

The use of two different classes of covalent organic frameworks (covalent triazine and imine linked frameworks) as supports for molecular Ni²⁺ catalysts is presented. For COFs, a large concentration of N heteroatoms, either in the form of *quasi* bipyridine or as diiminopyridine moieties, allows for the coordination of NiBr₂ to the scaffold of the porous polymers. When applied as catalysts in the oligomerization of ethylene under mild reaction conditions (15 bar, 50 °C), these new catalysts display an activity comparable to those of their homogeneous counterpart and a fivefold higher selectivity to C₆⁺ olefins. Accumulation of long chain hydrocarbons within the porosity of the COFs leads to reversible deactivation. Full activity and selectivity of the best catalysts can be recovered upon washing with dichlorobenzene.

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1. Introduction

α -Olefins in the C₄–C₂₀ range are of the utmost importance as they are valuable and versatile feedstocks and building blocks for a variety of products that people consume on a daily basis, i.e. detergents, plasticizers, polymers. Currently oligomerization of ethylene is the prevalent method for the synthesis of these olefins [1].

Existing commercial processes utilize homogeneous catalysts. The two-step Ziegler stoichiometric process (INEOS), the one-step Ziegler process (Chevron-Phillips (CP) Chemicals) and the Shell higher olefins process (SHOP) are among the most widely applied industrial production methods together with the Idemitsu and SABIC processes. The two-step and the one-step Ziegler processes use triethylaluminium as a catalyst and SHOP is catalyzed by nickel complexes, while Idemitsu and SABIC processes use a combination of Zr and alkylaluminium [2].

At the end of 1990s new efficient homogeneous catalysts were discovered and subsequently extensively studied. These are diimine and iminopyridine complexes of nickel, cobalt or iron in combination with alkylaluminium [3–14]. Though homogeneous catalysts in general show better performance, the use of a heterogeneous catalysts would be desired from a practical point of view, as it would ease catalyst handling and recycling and may result in enhanced selectivities to specially interesting products such as C₈ olefins. In this spirit, significant amount of research on heteroge-

neous catalysts has been performed in the past few decades. Among those were nickel-exchanged zeolites [15–24], Ni-MCM and Ni-SBA catalysts [25–33], supported NiSO₄ [34–41], supported NiO [42–48] and nickel-exchanged silica-alumina [49–53]. The most active Ni-exchanged zeolite [17] and silica-alumina catalysts [51] show the formation of mainly C₄–C₈ olefins, with high selectivity to butenes (circa 70%). Selectivity to higher olefins can be enhanced by using bigger pore materials such as Ni-MCM catalysts [30,32]. In all these cases, the formation of a minor amount of C₁₀⁺ olefins was also detected (<10%). Supported NiSO₄ catalyses ethylene dimerization with selectivity to butenes of 100% [37,39]. In case of supported NiO, at low temperatures (20 °C) the only products are butenes, and in contrast, when high temperatures (150–200 °C) and high pressures are used, selectivity to butenes decreases to 10–13%, while, particularly, the formation of C₆⁺ is enhanced.

From a design point of view, the immobilization of well optimized homogenous catalysts offers a number of advantages such as better selectivity control and metal utilization. This approach has been followed by several groups. In these works, diimine nickel complexes have been anchored to MCM-41 and MFS [54] and to hybrid silica [55], iminopyridine metal complexes have been supported on carbon nanotubes [56,57] and diimine, iminopyridine, and bis(imino)pyridine metal complexes have been immobilized into mica layered materials [58–62].

Catalysts supported on MCM-41, MFS and carbon nanotubes show a high activity in the polymerization of ethylene, while hybrid silica supported catalysts selectively form butenes of 100%. Another interesting and unique approach is reported by

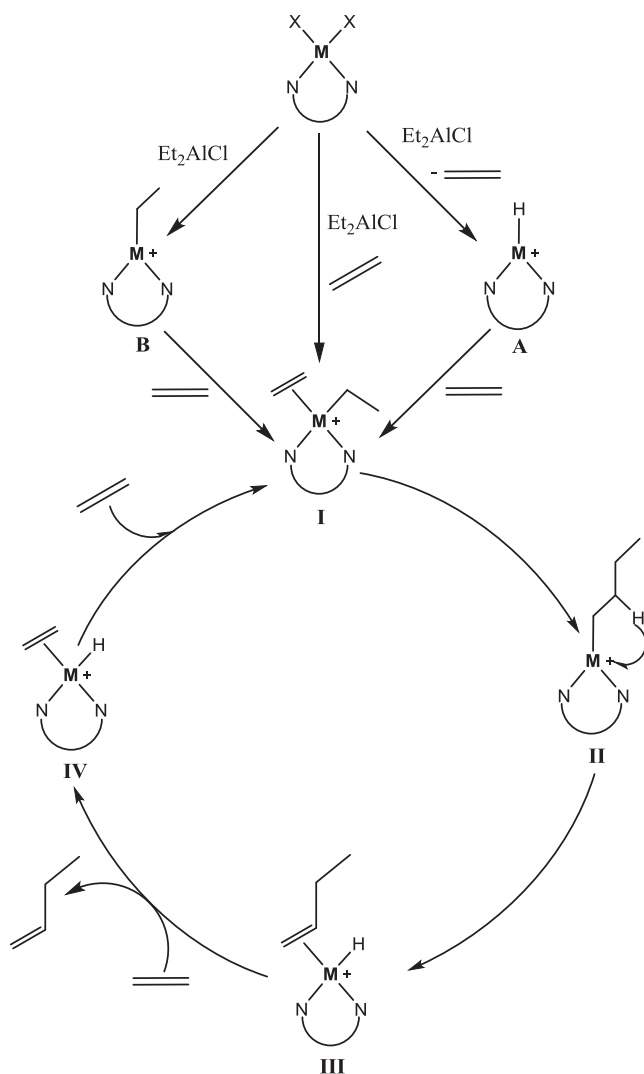
* Corresponding author.

E-mail address: j.gascon@tudelft.nl (J. Gascon).

Malgas-Enus et al., who used nickel metallodendrimers in a combination with alkylaluminium compound as catalyst, [63] reaching a maximum selectivity to butenes of 55%, with most of the other products being C₂₂–C₆₀ oligomers.

Recently, molecular heterogeneous catalysts based on Ni^{II} complexes supported on MOF materials were developed [64–69]. Another very interesting approach has been reported by Dinca's group by using a MOF support with a secondary building unit structurally homologous to 3-mesitylpyrazolyl Ni homogeneous catalysts [69]. In most cases, these catalysts display high selectivities to butenes (range from 85 to 95%) along with the formation of polyethylene on the surface of the catalyst [68].

The use of molecular catalysts requires the presence of a co-catalyst, alkylaluminium in most cases. According to the proposed reaction mechanisms [65,68,70,71] (Scheme 1), reaction with alkylaluminium has been proposed either to promote proton abstraction to active metal-hydride species (A), or to generate mono (B) or dialkylated (I) metal adducts. In case of metal-hydride or monoalkylated metal species, the next step is the insertion of ethylene to form a dialkylated adduct (I). Then the formation of an alkyl-metal intermediate (II) takes place that leads to intermediate IV after releasing butene through β -hydride elimination. Further inclusion of additional ethylene molecules on complex (II) yields



Scheme 1. Proposed mechanisms for ethylene oligomerization.

to the formation of higher olefins that are finally released via β -hydride elimination.

When looking at the reaction mechanism and at the examples summarized above, it is clear that prediction of the product spectrum of a given catalyst is not trivial, although, in general, it is proposed that stabilization of the first oligomerization product (III) at the surface of the catalyst is crucial in determining the “chain growth probability” of the process. In this line, hydrophobic supports seem to result in the production of a larger amount of longer olefins, while more hydrophilic supports mostly produce butenes.

In the light of the existing literature, we decided to explore the use of Covalent Organic Frameworks (COFs), more specifically, of Porous Aromatic Frameworks (PAFs), as potential supports for Ni ethylene oligomerization catalysts. PAFs consist only of light elements (C, N and H) and display a high degree of tunability, in terms of both pore size and surface area. In this spirit, we studied the use of two different families of PAFs: Covalent Triazine Frameworks (CTFs) with micro- and mesoporous structures, and a lamellar structured imine-linked polymer network (IL-PON). In both cases, a large concentration of N heteroatoms (either in the form of *quasi* bipyridine moieties in case of CTFs or in the form of diiminopyridine moieties in case of the IL-PON) within the porous structure of these materials allows for the direct coordination of Ni²⁺. Our results demonstrate that both families of solids hold great promise for the selective formation of C₈ olefins and that deactivation of the catalysts due to the adsorption of C₈–C₃₀ products can be easily mitigated by catalyst reactivation in dichlorobenzene.

2. Experimental section

2.1. Materials

1,3,5-Tris(4-aminophenyl)benzene was purchased from TCI Europe N.V. and used as received. All other reagents and solvents were purchased from Sigma-Aldrich and used as received.

2.2. Catalyst synthesis

2.2.1. Synthesis of imine-linked porous organic network (IL-PON)

The following general procedure was followed to prepare the IL-PON support: 116 mg (0.858 mmol) of 2,6-pyridinedicarboxaldehyde was dissolved in 10 ml of DMSO; 200 mg (0.569 mmol) of 1,3,5-tris(4-aminophenyl)benzene was dissolved in another 10 mL of DMSO. Then, solutions were mixed in a round-bottom flask and 1 mL of 99.8% acetic acid was added. Almost immediately there was a formation of the yellow polymer. Polymer was subsequently washed with methanol and THF and dried at 150 °C under vacuum giving 286 mg (yield based on the monomers ~90%) of a yellow powder.

2.2.2. Synthesis of mesoporous and microporous Covalent Triazine framework (meso-CTF and micro-CTF)

To synthesize microCTF, a glass ampoule was charged with 2,6-pyridinedicarbonitrile (0.124 g, 0.96 mmol) and anhydrous ZnCl₂ (0.664 g, 4.8 mmol) in a glovebox. For the mesoCTF, the ampoule was charged with 2,6-pyridinedicarbonitrile (0.041 g, 320 μ mol), 4,4'-biphenyldicarbonitrile (0.131 g, 640 μ mol) and anhydrous ZnCl₂ (0.664 g, 4.8 mmol). The ampoule was flame sealed and the mixture was heated at 500 °C for 48 h and then cooled to room temperature. The product was consecutively washed in 5 M HCl at 100 °C, in NH₄OH at 60 °C, in H₂O at 100 °C and then in THF at 60 °C, each step overnight. The washing steps might seem excessive, but were, as we found, required to remove ZnCl₂. Finally, the powder was dried in vacuum at 180 °C overnight.

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