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N-containing covalent organic frameworks as supports for rhodium as transition-metal catalysts in hydroformylation reactions

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ABSTRACT

Porous cross-linked polymers containing nitrogen donor functionalities are a promising class of materials for the immobilization of transition metal catalysts. These highly porous materials are built from ligand-containing building blocks using a bottom-up approach. Utilizing dinitrile containing monomers, highly porous covalent triazine frameworks (CTFs) are formed at elevated temperatures in molten zinc chloride. Containing a large number of accessible nitrogen coordination sites, metal species can be stabilized within these materials. The materials' porosity can be tuned, depending on the monomeric building block used and synthesis conditions. By immobilizing rhodium species within the framework followed by pre-activation, Rh@CTF materials are suitable as catalysts in the solvent-free hydroformylation of 1-octene. These Rh@CTF catalysts are not as active as conventional homogeneous benchmark catalysts; however, their activity and selectivity clearly outperform comparable carbon-based catalysts. A correlation between porosity and polarity of the support material and the observed catalytic activity could be established. Furthermore, CTF-based catalysts could be recycled easily with no further treatment for up to five runs with just a gradual deactivation. The leaching of active species has been studied intensively to elucidate the strength of the metal-support-interactions in this rather challenging reaction for an immobilized catalyst.

1. Introduction

During the last few years, the large gap between heterogeneous and homogeneous catalysts started to shrink and numerous concepts for immobilized homogeneous catalysts evolved. These catalysts aim at combining the major advantages of both systems e.g. easy separation as well as defined molecular species as active centers. Nevertheless, for most immobilized catalysts, characterization presents a challenge and several types of deactivation processes can occur. Consequently, it is essential to apply a support material that stabilizes the catalytically active species and is strong enough to prevent leaching, agglomeration or other types of deactivation.

Covalent triazine frameworks (CTF) are a type of covalent organic framework containing triazine-linked functionalized building blocks. Synthesized from dinitrile-based monomers in molten zinc chloride in an ionothermal reaction, a variety of highly porous polymer structures can be achieved. Unlike other covalent organic frameworks [1,2], these materials are stable against concentrated acids, organic solvents and high temperatures and show no swelling behavior in any kind of solvent. Within this work, we used 1,3-dicyanobenzene (CTF-a), 2,6-dicyanopyridine (CTF-b), 1,4-dicyanobenzene (CTF-c) and 4,4′-dicyanobiphenyl (CTF-d) for the framework synthesis. The polymerization of these linkers to form trimers or polymers in the presence of acidic metal catalysts has already been described in 1962 [3] and 1973 [4], respectively. However, Kuhn et al. discovered the potential of these porous materials for application in e.g. catalysis, separation and gas storage first in 2008 [5,6]. They used higher amounts of zinc chloride in the synthesis, which had to be removed by washing with water after synthesis to free up the formed porous structure. Furthermore, they applied different monomers within the polymerization and identified that it is crucial for defining the optimal synthesis conditions [5–9].

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The porosity and structure of CTF-materials can be altered by utilizing dinitrile-based starting materials with different structure and substitution or by applying different synthesis temperatures or times. Kuhn et al. pointed out that the substrate:zinc chloride ratio has a strong influence on the degree of polymerization, carbonization and degradation [6]. Nevertheless, the duration of polymerization exhibits the strongest influence on the polymerization degree and the formation of larger pores. For catalytic applications, we could recently demonstrate superior performance of materials polymerized for shorter periods [10].

Besides the high porosity, CTF-materials offer a large number of accessible nitrogen centers, which can be used to coordinate metal centers; these coordinated metals can afterwards be applied in catalysis. Platinum immobilized on CTF-b has been used for the low-temperature oxidation of methane in presence of sulfuric acid [11,12]. The catalytic system has been studied in detail to elucidate the active species and its coordinative environment [13]. For these catalysts it could be shown, that the active species are indeed stabilized by nitrogen centers resembling the structure of the homogeneous benchmark catalyst reported by Periana et al. [11,14].

Recently, it has been proposed that transition metal nanoparticles can be immobilized on CTF-materials as well. In this case, the nitrogen centers stabilize the metal nanoparticles to hinder agglomeration, particle growth and leaching [15]. Immobilized ruthenium and palladium particles have been used in the selective aerobic oxidation of 5-hydroxymethylfurfural. Depending on the reaction conditions 2,5-furan dicarboxylic acid or furandialdehyde can be formed selectively. In comparison to similar catalysts based on carbon supports, mesoporous CTF-based catalysts enabled superior activity and enhanced recyclability [10,16].

Hydroformylation is challenging for immobilized catalysts as both substrates, carbon monoxide and olefins, are good π-donor centers to build a strong Rh-complex with the immobilized metal centers resulting in a very stable homogeneous complex [17,18]. Consequently, sufficient stabilization of the metal centers within the material is necessary to prevent the formation of any homogeneous species. On an industrial scale, a two-phase system is applied. The commonly known Ruhrchemie-Rhône-Poulenc process, with rhodium centers immobilized in aqueous phase using a hydrophilic ligand, is a good example for the two-phase immobilization of homogeneous catalysts [19]. Other interesting strategies relate to supported-ionic-liquid-phase (SILP) catalysts to immobilize the catalyst within an ionic liquid layer on a suitable support material [20,21]. The main challenge of both concepts concerns the limited substrate range caused by the need for sufficient solubility of substrates and/or products in the stationary and the immobilized liquid phase.

Supported metal nanoparticles or immobilized catalysts might offer the opportunity to overcome this limitation and several systems have been reported [22–26]. To support rhodium nanoparticles, oxidic supports [24,25,27–29] or carbon-based materials [24] have been applied in this reaction. Further addition of homogeneous ligands to these catalysts facilitated tuning selectivity [30] or introducing stereo chemical information [23]. To increase the strength of the rhodium–support interactions, materials with ligand-like structures or ligands attached to the surface have been synthesized to form immobilized catalytically active species [26,31–33]. Despite promising results in these studies, metal leaching remains a major challenge for heterogenized catalyst systems used in hydroformylation. In this study, we apply CTF-based materials to overcome these limitations by stabilizing metal centers and metal nanoparticles via the nitrogen functionalities of these networks. Leaching has been studied in detail and used to indicate the strength of the coordinative stabilization offered by the nitrogen centers of the triazine framework.

2. Experimental

2.1. Materials

Zinc chloride (Aldrich, Redi-Dri™) and rhodium(III) chloride hydrate (Aldrich, Rh 38–40%) were stored in a glove box and used as received. 1,3-Dicyanobenzene (1,3-DCB), 2,6-dicyanopyridine (2,6-DCP), 1,4-dicyanobenzene (1,4-DCB), 4,4′-dicyanobiphenyl (4,4′-DCBP) and nonane (Fluca, analytical standard) were purchased from Aldrich and were used as received. 1-Octene (Aldrich, 98%) was dried over 4 Å molecular sieve and degassed prior to use. Toluene (technical grade) was purified by distillation, pre-dried over $CaCl_2$, dried and stored over 4 Å molecular sieve and degassed in a solvent purification system by Innovative Technology.

2.2. Synthesis of polytriazine networks (CTF)

The CTF-materials were synthesized after the following procedure, this is described elsewhere [5–7,11]. For CTF-a synthesis 1,3-dicyanobenzene (0.621 g, 4.85 mmol) and zinc chloride (3.300 g, 24.2 mmol) were ground and transferred into a quartz ampule (15 × 100 mm) within an inert atmosphere. The ampule was evacuated, sealed and heated to 400 °C for 10 h and 600 °C for 10 h. The ampule was afterwards cooled down to room temperature and opened. The resulting solidified black melt was washed with dilute aqueous hydrochloric acid and deionized water until a coarse granulate remained. This granulate was ground using a ball mill (Fritsch Pulverisette 23 for 5 min at 30 Hz) and stirred in dilute aqueous solution of hydrochloric acid for 20 h. The resulting fine powder was washed with deionized water, THF, and dilute sodium hydroxide, and dried in vacuum at 80 °C. CTF-b, CTF-c and CTF-d were synthesized as mentioned for CTF-a.

2.3. Immobilization of rhodium species

To an aqueous rhodium(III) chloride hydrate solution ($c_{Rh} = 0.01$–0.04 g/L) the CTF-material (0.5–1 g/L) was added and the suspension was stirred for 12–72 h at 750 rpm. After filtering off the material, it was washed with deionized water. The amount of coordinated metal species was determined by ICP-OES analysis of the metal solution (a) prior to the addition of CTF, (b) after filtering off the material and (c) of the washing solution.

2.4. Catalyst pre-activation

Prior to the catalytic application, the Rh-containing CTF material was reduced in a H_2-flow of 5 L/h at 250 °C for 3 h. During the heating-up and cooling-down period an Ar-flow of 5 L/h was applied. After reduction the catalyst was handled under inert gas atmosphere. It became apparent that after being exposed for longer times with air, Rh@CTF materials showed higher tendencies of leaching.

2.5. Catalytic reactions

Catalyst and 1-octene (dried and degassed) were mixed within a glass inlet of a 75 mL custom-built stainless steel autoclave equipped with a magnetic stirring bar. After this autoclave had been closed and sealed, it was flushed with argon and syngas ($CO:H_2 = 1:1$) and pressurized with syngas to the desired pressure. The system was afterwards heated up to the desired temperature by an external electrical heating jacket and stirred by a magnetic stirrer during the reaction. After cooling the reactor to r.t. and releasing the pressure, the catalyst was removed using a Whatman® filter system equipped with an Anodisc 25 glass membrane under Ar-atmosphere, washed with toluene (dry, degassed) and