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Magnetic Core–Shell Nanoparticles as Carriers for Olefin Dimerization Catalysts

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We report the covalent support of functionalized nickel complexes on magnetic core–shell hybrid particles γ -Fe_2O_3/SiO_2. Two completely different ways of connecting the particle with these nickel complexes were carried out. The first approach used the hydrosilylation method between the alkene-substituted nickel complex and a silane. In a second approach, the particles were connected with the complexes by

means of click chemistry (copper-catalyzed Huisgen 1,3-dipolar cycloaddition). For this purpose, the nickel complexes were substituted with an alkyne moiety. Transmission and scanning electron microscopies, energy-dispersive X-ray diffraction, and FTIR spectroscopy were the methods employed to characterize the successful heterogenization of the nickel complexes.

Introduction

Nanotechnology is a multidisciplinary platform to target materials for a wide field of applications. Magnetic nanoparticles and hybrid core–shell particles of well-defined size and shape with unique and advanced properties for a large field of possible applications have received a great deal of attention that range from biomedical applications, magnetic separation media, and other high-functional devices^[1–5] to materials engineering^[6–10] and catalysis.^[11–17] A spherical nanoparticle with a core–shell architecture is a viable way to combine multiple functionalities on a nanoscopic scale.^[18–20]

Catalysis is becoming a strategic field of science because it represents a new way to meet the challenges in many different fields. The concept of green chemistry, which makes catalysis science even more important, has become a routine part of sustainable chemistry and daily life. Nanocatalysts with tunable size, shape, and composition have drawn tremendous interest in both theoretical and technological fields in recent years.^[21,22] Although heterogeneous catalysts are widely used in a variety of industries, it is often difficult to isolate and separate the final product after the reaction has completed. Homogeneous catalysis suffers from the problematic separation of the catalysts and prod-

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ucts, and the reuse of the catalyst. These problems are of environmental and economic interest in terms of large-scale synthesis. A possible heterogenization of the existing catalysts could help to design nanocatalysts with excellent activity, greater selectivity, and higher stability, and could be an attractive solution to this problem. These characteristics can easily be achieved by means of tailoring the size, shape, morphology, composition, and thermal and chemical stability. The pioneering compounds of magnetochemistry are superparamagnetic iron oxide particles, such as magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃). In addition to these oxide materials, pure metal nanomagnets made out of iron or cobalt are producible on relevant scales.^[23-26] Both blank particles are vulnerable to the loss of magnetism in chemical reactions. For further applications, the particles need to be protected against chemical, thermal or mechanical influences. In general, there are three methods of stabilization: (1) the addition of monomers such as carboxylates or phosphates,^[27-30] (2) coating with inorganic materials such as silica or gold metal,^[31–36] and (3) coating with organic matrices such as surfactants and polymers.^[37-42] Silica plays an important role in the preparation of core-shell nanoparticle systems due to its excellent physical and chemical properties, its variable surface chemistry, and its drastically increased chemical stability. It is optically transparent, easily functionalized, and the simple and robust synthesis of silica particles from the monomer tetraethoxysilane (TEOS) has been established for many decades. Silica-coated y-Fe₂O₃ magnetic nanoparticles (MNPs) combine the advantages of magnetic cores and silica surfaces that can be functionalized. Although classic heterogeneous catalysts are widely used in industry, lower activities than homogeneous systems are commonly detected.^[42] A great proportion of these catalysts are deep inside the supporting material and thus reac-





tants have limited access to the catalytic sites.^[43] By decreasing the size of the support down to the nanometer scale, the surface area is increased and the support can be evenly dispersed in solution, thereby forming a homogeneous emulsion.^[13] In recent years, much attention has been focused on catalysis research, and magnetic nanoparticles have been employed in important reactions such as hydrogenation, hydroformylation, Suzuki–Miyaura and Heck couplings, and olefin metathesis.^[44–46]

Herein, we combine the properties of core-shell nanoparticles with the catalytic character of certain complexes in hybrid core-shell-corona nanoparticles. The idea was to create a heterogeneous catalyst for facile product separation for the catalytic conversion of olefins. An external magnet can remove the magnetic particles from the solution, or generate two phases for subsequent product separation. We report the application of nickel complexes supported on magnetic nanoparticles incorporated into silica shells during the catalyzed polymerization and dimerization of both ethylene and propylene.

Results and Discussion

Here we describe in detail the synthesis, characterization, and catalytic behavior of the catalysts on magnetic coreshell nanoparticles (NPs). The synthetic strategy towards monodisperse hybrid catalysts with core-shell architecture consists of the following steps. In a first step, we synthesized monodisperse and hydrophobically functionalized superparamagnetic γ -Fe₂O₃ NPs by means of the thermal decomposition of [Fe(CO)₅] in the presence of oleic acid, which serve as cores for the final hybrid particles (Figure 1, A). Afterwards single NPs were encapsulated with a silica layer by a dedicated microemulsion procedure, thus yielding monodisperse core-shell γ -Fe₂O₃/SiO₂ particles. Precise adjustment of the conditions allows one to achieve a reliable encapsulation and to either entrap several particles or individual ones and to precisely tailor the thickness of the silica shell.^[10] The size of the γ -Fe₂O₃ particles is sufficiently controlled by the amount of oleic acid that is used in relation to the amount of [Fe(CO)₅]. TEM images in Figure 1 (A) show the γ -Fe₂O₃ cores with an average diameter of (9.9 ± 1.8) nm, which is corroborated by dynamic light scattering (DLS) with a *z*-average hydrodynamic radius of 6.6 nm and a polydispersity index (PDI) of 0.04. Clearly, the oleic acid ligand shell is invisible in the TEM image, but contributes to the hydrodynamic distribution function obtained by DLS, thus resulting in a higher value.^[5] A thin 20 nm layer of silica was coated on this core by means of a sol–gel process to give silica-coated γ -Fe₂O₃ magnetic nanoparticles with an average diameter of 52 nm (Figure 1, B).

The series of catalysts (Scheme 1) was designed to include two methods of linkage with the core-shell support material. Both methods contain simple reaction steps and uncomplicated handling and anchoring of a triethoxysilane group. As will be mentioned in the Experimental Section, the first approach (Scheme 2/3) uses hydrosilylation to combine the bis(imine)nickel complex with the supporting material. The second approach (Scheme 4) describes the combination of the azido-functionalized magnetic particles and the alkyne end-functionalized phenoxyimine–nickel complexes by using copper-catalyzed azide–alkyne Huisgen 1,3dipolar cycloaddition (CuAAC).^[47,48] For both approaches, the same magnetic core–shell particles that contain a γ -Fe₂O₃ core coated with a silica layer were used.

The first synthetic strategy involves a precursor that consists of an ω -alkenyl diimine moiety coordinated to nickel(II) bromide and a silane that can react with the silica particles (Scheme 2). After the silane-ene reaction, the complex with the triethoxysilane moiety can be coupled directly to the support material (Scheme 3). This hydrosilylation reaction is simple and quick. After heating in toluene, com-



Figure 1. TEM images of (A) the iron oxide cores and (B) the magnetic nanoparticles with silica shell. (C) Intensity-weighted hydrodynamic radii distribution (DLS) of γ -Fe₂O₃ (–) and γ -Fe₂O₃/SiO₂ (--).



Scheme 1. Prepared complexes 2-4 containing an alkyne moiety.



Scheme 2. Hydrosilylation reaction of the diimine nickel complex and triethoxysilane.



Scheme 3. Route of heterogenization for complex 1.

plex 1 was immobilized covalently on the silica support (1-H). Following the product removal by centrifugation, the particles were washed with toluene, THF, and CH₂Cl₂.

TEM images in Figure 2 show the core-shell structure with the modified surface of the particles. The surface of the particles with connected complexes is distinctly coarser



than the blank Fe_2O_3/SiO_2 nanoparticles. This indicates that a thin layer of supported catalyst surrounds the silica particles.



Figure 2. TEM image of 1-H. The surface is distinctly coarser than the blank particles.

Energy-dispersive X-ray diffraction (EDX) was used to identify the chemical composition at the surface and of the particles. The EDX spectrum in Figure 3 clearly shows the typical peaks. A small peak from the iron core is clear. Silicon (shell) and oxygen (core and shell) are the dominant peaks. This can be confirmed by peak integration of the typical nickel and bromine peaks, which shows a 4.2 and 7.9% fraction, respectively. This represents an atomic ratio of 1:1.9, thus confirming the composition NiBr₂. These results are in good agreement with the proposed structure and the conclusion drawn from the TEM image.



Figure 3. EDX spectrum of the heterogeneous complex 1-H.

In the second approach (Scheme 4), we discuss the heterogenization of phenoxyimine–nickel complexes. Here, Huisgen 1,3-dipolar cycloaddition is used to attach azido-functionalized γ -Fe₂O₃/SiO₂ particles to the alkyne group of the complex. This is a very adaptable method to attach any compound that carries an alkyne group to a desired surface. Therefore, three different nickel complexes that bear an alkyne group (Scheme 2) were synthesized and con-



Scheme 4. Route of heterogenization for complexes 2-4.



nected to the azido-functionalized support by following the procedure shown in Scheme 4. The respective ligands were synthesized according to the literature,^[49] and the complexes were obtained through a known process.^[50] The magnetic particles Fe_2O_3/SiO_2 were combined with an azide-functionalized propyl(triethoxy)silane moiety through condensation. Huisgen 1,3-dipolar cycloaddition was used to attach azido-functionalized γ -Fe₂O₃/SiO₂ particles to the alkyne group of the complex. Figure 4 shows the FTIR spectra of the pure γ -Fe₂O₃/SiO₂ (2-H), and pure complex 2. The silica surface is characterized by two dominant peaks: the nonbonded surface Si–OH groups with a band in the range of 3300–3700 cm⁻¹, and the characteristic Si–O–Si vibration (1080 cm⁻¹).



Figure 4. FTIR spectra of the pure nanoparticles (MNP), the supported complex (2-H), and the corresponding pure complex (2).

The supported complex shows two peaks at 1620 and 1730 cm⁻¹, which are typical for the C=N and C=C stretching bands. The created triazole group shows a typical peak at 1450 cm⁻¹ that is dominated by the peaks of the support. This resonance is not very intense, but it is the only characteristic resonance of the triazole group and confirms a successful grafting. The phenoxyimine complex unit itself shows no strong IR stretching frequency and it is likely masked by the silica bands of the support. The pure complex shows the very intense band of the C–H vibration of the alkyne group (3280 cm⁻¹).

After the click reaction with the alkyne complexes, the particles were imaged by TEM. Figure 5 shows the core-shell structure with the modified surface of the particles.

The surface of the heterogeneous complexes is distinctly coarser than the blank γ -Fe₂O₃/SiO₂ particles. All these aspects indicate that the heterogenization reaction was successful, and the IR results are confirmed.



Figure 5. TEM image of **2-H**. The surface is distinctly coarser than the blank particles.

Catalytic Properties

The catalytic performance of the heterogeneous catalysts 1-H, 2-H, 3-H, and 4-H is described in the following section. The bisimino-nickel complex 1-H was applied as catalyst for the catalytic polymerization of ethylene. Recent works have described the homogeneous polymerization of ethylene with bisimino-nickel complexes after activation with methylaluminoxane (MAO).^[39] In our experiments, the immobilized catalyst was stirred in toluene, and ethylene was added to the solution under low pressure for 20 min. After quenching with 2-propanol, the polymer particles were washed and separated by means of centrifugation. The particles were visualized by SEM (Figure 6). The images show spherical particles with a rough polymer surface. A broad polymer particle-size distribution with particle sizes from 0.1 to 1.5 µm was observed. The images show that polymerization happens at the catalysts on the particle surface and that the particles grow independently.



Figure 6. SEM images of the polyethylene particles polymerized by **1-H**.

The polymerization test proves that covalently immobilized complexes on γ -Fe₂O₃/SiO₂ particles are catalytically



FULL PAPER

active and that catalysis happens at these functionalized particles. The polymerization experiments were carried out as control experiments for the following dimerization experiments, in which no change in the shape and size of the catalytic active particles could be observed. During the catalytic tests, we mainly focused on the role of the support in easing the product separation. Thus, all catalytic tests were carried out using a heterogeneous catalyst in a closed system (pressure Schlenk tube). Here, we used phenoxy-imine–nickel complexes (2-H), which are normally highly active for the dimerization of propylene after activation with MAO.

With two ligands coordinating the central metal, the phenoxyimine complexes have two sides for heterogenization (Scheme 5). After activation with MAO, one ligand leaves the complex and leaves a free coordination side. After activation, a single complex is fixed on a single side to a particle. The catalytic dimerization of propylene was performed with all three immobilized catalysts. Whereas bisimine–nickel catalysts are known for their catalytic polymerization of ethylene,^[39] phenoxyimine–nickel complexes are highly active for the dimerization of propylene.^[41]



Scheme 5. Phenoxyimine–nickel complexes before and after activation with MAO. The square represents the free coordination site. $^{[51]}$

The results in Table 1 show products of the dimerization reactions of the supported catalysts 2-H, 3-H, and 4-H after activation with MAO. All three heterogeneous catalysts show high selectivities of up to 92% for dimeric products. In addition to some trimeric products, nearly no higher oligomers are formed. Aside from all the general advantages of heterogeneous catalysts that have already been mentioned, the activity of our heterogeneous catalysts is comparable to their homogeneous analogues.^[50] Table 1 shows the dimerization results of the heterogeneous catalysts. The catalytic activities are in the range of 264 to 405, which represents turnover numbers (TONs) of 3150 (2), 4520 (4), and 4820 (3). The gas chromatograms of the dimerization experiments show typical distribution. The branched methylpentenes t-4-MP-2 (trans-4-methyl-pent-2ene) and 2-MP-2 (2-methylpent-2-ene) are the main products, with 4-MP-1 (4-methylpent-1-ene), c-4-MP-2 (cis-4methylpent-2-ene), t-2-Hex (trans-2-hexene), and c-2-Hex (cis-2-hexene) as byproducts.

Table 1. Results of the catalytic dimeri	zation of propylene with the
heterogeneous complexes 2-H, 3-H, ar	nd 4-H .

	C6 [%]	C9 [%]	C12 [%]	Activity of the heterogeneous catalyst [kg(product)/mol h ⁻¹]
2-Н	75	25	_	264
3-Н	92	6	2	405
4-H	87	7	6	380

All three heterogeneous catalysts are highly efficient for the catalytic dimerization of propylene (Table 1). The catalytic activities and the product distribution are in a range that agrees with the literature.^[41] The reaction products were decanted after separating the particles by using a strong magnet to hold the catalyst in the Schlenk tube.

Conclusion

We have demonstrated the successful heterogenization of phenoxyimine-nickel and bis(imine)-nickel complexes by means of an azide-alkyne click reaction and hydrosilylation reaction. Uniformly nanosized silica-coated magnetic nanoparticles were synthesized and used as support material. The complexes were covalently bound to the silica shell, according to EDX, TEM, and FTIR observations. Polymerization of ethylene after activation with MAO was successful and SEM images clearly show spherical particles with a rough polymer surface. Dimerization of propylene showed the excellent catalytic properties of the heterogenized phenoxyimine-nickel complexes. The compared use under homogeneous "free" conditions resulted in the same product distribution. The facile preparation and the catalytic properties show the high potential of this heterogeneous system. Catalysts can be separated by means of a strong magnet, and ease the problematic product separation. The application of this catalytic system combines homogeneous activities and selectivities, and the separation of the product and the catalyst phase in heterogeneous systems.

Experimental Section

General Considerations: Air- and moisture-sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk or glovebox techniques. The dimerization reactions were performed with pressure Schlenk tubes.

Materials: All solvents were purchased as technical grade and purified by distillation over Na/K alloy under an argon atmosphere. Iron(0)pentacarbonyl {[Fe(CO)₅]; 99.9%}, oleic acid (90%), dioctyl ether (> 99%), poly[oxyethylene(5)]nonylphenyl ether (Igepal CO-520), ammonium hydroxide (NH₄OH; 28% in H₂O), and tetraethylorthosilicate (TEOS; >98%) were purchased from Sigma Aldrich. All other chemicals were purchased commercially from Aldrich or Acros or were synthesized according to literature procedures. The MAO solution (30 wt.-% in toluene) was obtained from Albemarle, USA.

Procedure for the Synthesis of γ -Fe₂O₃ Nanoparticles: The synthesis of γ -Fe₂O₃ nanoparticles was adapted from the literature.^[5,10] A



250 mL two-neck round-bottomed flask, connected to a reflux condenser, was charged with dioctyl ether (120 mL) and oleic acid (29.0 mL, 25.76 g, 91.2 mmol) and degassed with N₂ for 15 min. The reaction mixture was heated to 100 °C under an N₂ atmosphere before [Fe(CO)₅] (4 mL, 30.4 mmol) was added. Subsequently, the resulting mixture was heated to reflux and was kept for 1.5 h until the solution turned black. After cooling to room temperature, the reaction mixture was stirred under air to initiate the oxidation process of iron to achieve γ-Fe₂O₃ nanoparticles. The resulting particles were precipitated with ethanol and separated by means of an NbFeB magnet. The particles were immediately redispersed in toluene, THF, or *n*-hexane. For further purification, the precipitation and separation process was repeated.

Procedure for the Synthesis of γ -Fe₂O₃/SiO₂ Core–Shell Particles: The synthesis is based on the experimental procedure mentioned in the literature.^[10] Herein, we present detailed experimental conditions. Polyoxyethylene(5)nonylphenyl ether (0.23 g, 0.54 mmol, Igepal CO-520) was dispersed in a 10 mL small flask that contained cyclohexane (4.5 mL) in a ultrasound bath for 10 min. Next, y-Fe₂O₃ nanoparticles dispersed in cyclohexane (400 µL. 0.5 mgmL⁻¹) were added to the flask and vortexed for 5 min at 200 min⁻¹. The rapid addition of ammonium hydroxide (29.4%, 40 µL) formed a reverse brownish microemulsion, and the subsequent addition of tetraethylorthosilicate (30 µL) started the growth of the silica shell. The nanocomposite particles were aged for 48 h by using a shaking incubator at room temp. and at 100 rpm as the oscillation rate (soft agitation). Then they were purified by several cycles of centrifugation at 4500 rpm for 10 min and cautious redispersion in ethanol. The magnetic core-shell particles could also be magnetically collected. The final product was redispersed in millipore water.

Procedure for the Synthesis of the Complexes

Complex 1 was prepared and characterized elsewhere.^[52] For compounds 2, 3, and 4, the respective ligand precursor (10 mmol) in ethanol (100 mL) was mixed with Ni(OAc)₂·xH₂O (5 mmol) (Scheme 1). The solution was stirred under reflux for 24 h. The volume was reduced and the complexes precipitated by the addition of pentane. The products were filtered through a glass frit and washed with pentane. The complexes were obtained as green solids with yields in the range of 73–82%. Similar complexes were first described by Dieck et al. and are known as polymerization catalysts in combination with MAO.^[53]

MS data for 2: m/z (%) = 608 [M⁺⁺] (68), 357 (9), 333 (72), 236 (100). C₃₂H₃₄Cl₂N₂NiO₂ (608.25): calcd. C 63.19, H 5.63, N 4.61; found C 63.08, H 5.52, N 4.53.

MS data for 3: m/z (%) = 485 [M⁺] (37), 214 (100). C₂₈H₃₁N₂NiO₂ (486.28): calcd. C 69.16, H 6.43, N 5.76; found C 69.64.08, H 6.31, N 5.47.

MS data for 4: m/z (%) = 610 [M⁺⁺] (41), 510 (41), 335 (27), 276 (100). C₃₈H₃₆N₂NiO₂ (611.42): calcd. C 74.65, H 5.93, N 4.58; found 74.17, H 5.34, N 4.81.

Synthesis of the Supported Complexes: These core–shell particles contain an γ -Fe₂O₃ core coated with a silica layer. The silica shell has plenty of hydroxy groups for potential derivatization, on which the catalysts can be successfully immobilized. The series of catalysts was designed to include two methods of linkage with the core–shell support material. Both methods contain simple reaction steps and uncomplicated handling and anchoring of a triethoxysilane group. The first approach (Schemes 2 and 3) uses hydrosilylation to combine the bis(imine)–nickel complex with the supporting material. The second approach (Scheme 4) describes the combination of the

magnetic particles and the alkyne end-functionalized phenoxyimine–nickel complexes by using the copper-catalyzed azide–alkyne Huisgen 1,3-dipolar cycloaddition (CuAAC).

Approach 1: To obtain 1-H, complex 1 (630 mg, 1.28 mmol) was dissolved in a minimum amount of toluene. Speier's catalyst (H₂PtCl₆; 5 mg, 12 μ mol) was added. Triethoxysilane (233 mg, 1.42 mmol) was added dropwise over a period of 30 min. After 24 h of stirring, the complex precipitated by the addition of pentane (Scheme 2). The solution was removed, and the magnetic core–shell nanoparticles (100 mg) in toluene (25 mL) was added. The suspension was stirred for 3 d at 85 °C. The slight blue solution was separated from the brown-green solid, and the particles were thoroughly washed with toluene, THF, and CH₂Cl₂ (Scheme 3).

Approach 2:^[47–50] To obtain **2-H**, **3-H**, and **4-H**, chloropropyl(triethoxy)silane (8.8 g) and sodium azide (2.4 g) were stirred in DMSO (100 mL) for 4 d. A white solid precipitated and was removed by filtration. The magnetic particles (200 mg) were added to a third of the solution and stirred for 4 d at 80 °C. The particles were separated and suspended in toluene with an excess amount of the respective catalysts (1 g). Copper chloride (2 mg) and sodium ascorbate (4 mg) were dissolved in distilled water (5 mL) and added to the stirred mixture. After a reaction time of 4 d, the particles were separated by means of centrifugation and washed thoroughly with toluene, ethanol, and pentane.

Polymerization of Ethylene: The supported catalyst (25 mg) was placed in a pressure Schlenk tube with toluene (10 mL) and MAO solution (12 mL, 10 wt.-%). Ethylene was added under pressure (2 bar) for 20 min at room temperature. The particles were carefully washed with 2-propanol and toluene, and separated from the solution and dried under vacuum.

Dimerization of Propylene: The supported catalyst (25 mg) was placed in a 400 mL pressure Schlenk tube with toluene (5 mL) and activated with MAO solution (10 mL; Ni/Al 1:500). The pressure Schlenk tube was filled with liquid propylene (50 mL) and closed, warmed to room temperature with an external water bath, and stirred. After a reaction time of 1 h, the Schlenk tube was opened and the solution was analyzed by GC.

Characterization: The products of the dimerization experiments were characterized with a gas chromatograph (Agilent 6890) and GC/MS instrument (FOCUS DSQ Thermo Scientific). Mass spectra were recorded with a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70 eV). Elemental analyses were performed with a VarioEl III CHN instrument. Acetanilide was used as standard.

Bright-field TEM was performed with Zeiss CEM 902 and LEO 922 OMEGA electron microscopes operated at 80 and 200 kV, respectively. Data evaluation and processing was carried out with Soft Imaging Viewer and Image Tool. SEM was performed with a LEO 1530 Gemini instrument equipped with a field-emission cathode with a lateral resolution of approximately 2 nm. The acceleration voltage was chosen between 0.5 and 30 kV for energy-dispersive X-ray analysis (EDX). EDX spectra were measured with a LEO 1530 Gemini instrument and an Oxford EDX INCA 400 device. The obtained spectra were analyzed with the microscope software and the present elements in the sample were detected by their corresponding X-ray absorption peaks.

FTIR was carried out with a Spectrum 100 FTIR spectrometer from Perkin–Elmer. For measurements, a U-ATR unit was used. The dried samples were directly placed on top of the U-ATR unit for measurements.



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