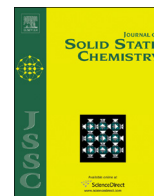




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Ligand-tailored single-site silica supported titanium catalysts: Synthesis, characterization and towards cyanosilylation reaction



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ABSTRACT

A successive anchoring of $\text{Ti}(\text{NMe}_2)_4$, cyclopentadiene and a O-donor ligand, 1-hydroxyethylbenzene (PEA), 1,1'-bi-2-naphthol (Binol) or 2,3-dihydroxybutanedioic acid diethyl ester (Tartrate), on silica was conducted by SOMC strategy in moderate conditions. The silica, monitored by *in-situ* Fourier transform infrared spectroscopy (*in-situ* FT-IR), was pretreated at different temperatures (200, 500 and 800 °C). The ligand tailored silica-supported titanium complexes were characterized by *in-situ* FT-IR, ^{13}C CP MAS-NMR, X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) and elemental analysis in detail, verifying that the surface titanium species are single sited. The catalytic activity of the ligand tailored single-site silica supported titanium complexes was evaluated by a cyanosilylation of benzaldehyde. The results showed that the catalytic activity is dependent strongly on the dehydroxylation temperatures of silica and the configuration of the ligands.

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1. Introduction

Heterogeneous and homogeneous catalysis are both the most common branches in the realm of catalytic systems [1]. However, the presences of different active species or their low concentration in heterogeneous catalysts impedes the development of better catalysts [2]. On the other hand, drawbacks of more by-products and shorter catalyst life due to easy inactivation occur usually in homogeneous catalysis. Therefore, it is necessary to develop an efficient strategy to overcome all those disadvantages and even combine the advantages of both areas. For meeting this challenge, surface organometallic chemistry (SOMC) has been developed as a unique approach for catalyst design, which produces highly active catalytic surface sites that are easily accessible and controlled [3]. The major achievement in this field was made mainly by Basset and his group. It has been enabled to obtain "single-site" catalysts for various known or even new catalytic reactions. For examples, alkane or olefin metathesis [4,5], polymerization [6], ethylene transformation [7], etc.

Transition metal-based SOMC is to achieve molecularly well-defined catalytic single sites, aiming to obtaining superior catalytic performance and facile reactivity control [3]. A large range of

metals such as Ti and Zr, [8], and other metals [9–12] have been served in this area. It is a remarkable fact that 4-coordinate electron-deficient Ti centers can expand their coordination to O-ligands or substrates and to activate O-ligands towards attack by electron-rich substrates. Therefore, among these transition metals, isolated Ti centers dispersed onto or within SiO_2 frameworks are active catalysts for a few reactions [13–16]. Corma [17], Thomas [18–20], and other groups [21–25] were quick to appreciate the advantages that large-pore silica would confer in facilitating the preparation of single-site, metal ion-centered heterogeneous catalysts. In this researches, the single-site surface active species was obtained successfully, whilst the di-, and tripodal species coexisted, which would affect the activity and selectivity of the catalytic reactions [2]. Higher dehydroxylation temperature was therefore indispensable for ensuring the lower density of isolated silanols for achievement of the single-site surface active species. The decrease of the isolated silanols density, however, gave rise to the decrease of the concentration of active site species and thus lowering of the catalytic activity of reactions. On the other hand, the higher pretreatment temperature could cause skeleton destruction of some supports such as MCM-41 [26]. An efficient strategy was therefore developed using ligands with large steric hindrance for synthesis of high density single-site surface species on the surface of the supports, which were pretreated at a lower dehydroxylation temperature [27]. This strategy provided a convenient way for introducing active centers on the surface of carriers, aiming to controlling either their distribution in the final materials or

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structures of the surface species, avoiding formation of di-, and tripodal species. For examples, Thomas [28,29] have taken advantage of the strong hydrogen bonding that secures tripodal attachment of an ionic (or zwitterionic) complex to a silanol-rich silica surface through a triflate [30] or a sulfonate tail [31]. McKittrick and Jones [32], Iglesia [33] and Katz [34] showed that preparing an isolated titanium-centered polymerization catalyst, and grafting calixarene–Ti complexes on silica to afford isolated 4-coordinate Ti species, respectively.

Recently, we are focusing on generating ligand-tailored single-site materials by SOMC method. We examined the relationship between density of silanol groups and pretreatment temperature to obtain optimal anchoring conditions. The strategy is to select a few O-donor ligands, including monodentate 1-phenylethanol (PEA), bidentate 1,1'-bi-2-naphthol (Binol) and 2,3-dihydroxysuccinic acid (Tartrate), to form ligand-tailored surface species on silanol-isolated silica. These species have the large steric hindrance which is beneficial to site isolation. On the other hand, we expected to enhance both conversion and selectivity in catalytic reactions by using the different monodentate or bidentate active group in the ligands, and their rigid or flexible structure. A variety of silica supported titanium complexes with the three different ligands were therefore synthesized and characterized. In search for the effect of surface structures on catalytic activity, cyanotrimethylsilylation of benzaldehyde with diverse ligand-tailored catalysts was investigated. The ligand-tailored strategy can obtain accessible, isolated, and structurally well-defined active sites, which will help us to understand the catalytic mechanism and verify active species onto the surface of a support in heterogeneous catalysis.

2. Experimental

2.1. General procedures

All experiments were carried out in a dry and oxygen-free argon environment by using the standard Schlenk-line or a glove box, toluene and hexane were distilled over Na/benzophenone and stored under argon over 4 Å molecular sieves and degassed prior to be used. 1,1'-bi-2-naphthol (Binol), 2,3-dihydroxysuccinic acid (Tartrate), 1-phenylethanol (PEA) and $\text{Ti}(\text{NMe}_2)_4$ (99.999%) were purchased from Aldrich. Benzaldehyde and trimethylsilyl cyanide (TMS-CN) were obtained from Alfa Aesar. All the reagents were used as received.

2.2. Preparation of catalysts

2.2.1. Preparation of ligand-tailored silica-supported Ti modified catalysts by impregnation

The Silica used in this work was purchased from Qingdao Haiyang Chemical Co., Ltd. Its parameters are: porosity=0.77 mL/g, BET=500, average pore size=5 nm. These parameters have no significant change under treatment at high temperatures: the BET specific surface areas and porosity are 480 m²/g and 0.76 mL/g for SiO_{2-200} , 495 m²/g and 0.75 mL/g for SiO_{2-500} , 490 m²/g and 0.74 mL/g or SiO_{2-800} . Taking the preparation of SiO_{2-500} -supported catalyst as an example, preparation procedure was performed in an oven connected to a Schlenk-line. SiO_2 (ca. 1.0 g) was pretreated at 500 °C under oxygen atmosphere for 8 h and then kept at 500 °C under high vacuum (10^{-3} Pa) for another 16 h to afford a dehydroxylated SiO_2 (SiO_{2-500}). $\text{Ti}(\text{NMe}_2)_4$ (15.0 μL , Ti, 0.063 mmol), *n*-hexane (20.0 mL), cyclopentadiene (Cp) (5 mL, 0.12 mmol Cp in toluene) and a O-donor ligand (Binol, PEA or Tartrate, 0.12 mmol) were mixed with SiO_{2-500} under vigorous stirring at room temperature for 16 h. The suspension was filtered and the residue was

washed with toluene (3×50 mL) and then pentane (3×50 mL). The solid was dried under vacuum (10^{-3} Pa) overnight and 1.064 g yellow powder was collected. The details for pretreatment of silica at 200 °C (SiO_{2-200}) and 800 °C (SiO_{2-800}) are in supporting information (SI).

2.3. Catalyst characterization

Elemental analysis and the X-ray photoelectron spectroscopy (XPS) were used for determination of Ti, N, C content in the samples. Elemental analysis was performed on a Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Germany). XPS analysis was performed using α Kratos AXIS-165 surface analysis system with a monochromatic AlK α radiation as the excitation source. Collected XPS spectra were analyzed using Thermo Avantage. All spectra were calibrated using the adventitious C 1s peak with fixed value of 284.6 eV. The X-ray absorption near edge structure (XANES) experiments was performed at the XAFS station (Beamline 4W1B) of the Beijing Synchrotron Irradiation Facility (BSRF) with stored electron energy of 2.2 GeV and ring currents between 160 and 250 mA. All of the data were collected in a transmission mode at room temperature with sampling was monochromatized using a Si (3 1 1) double-crystal monochromator. The intensities of the incident and transmitted beams were monitored using two N₂ and 50% argon-doped N₂-filled ionization chambers, respectively. The data treatment was carried out using the WinXAS2.0.

2.3.1. IR experiment

IR experiments were carried out on a Bruker Tensor 27 FT-IR spectrometer with a DTGS detector, using *in-situ* infrared cell equipped with CaF₂ windows. 32 Scans were accumulated for each spectrum (resolution is 4 cm⁻¹). A pretreated SiO_2 powder (0.15 g) was pressed into a disk, fixed in the *in-situ* IR reactor, and then moved to the bottom of the *in-situ* IR reactor smoothly for thermal treatments (dehydroxylation at different temperature: 100–800 °C. After dehydroxylation, the $\text{Ti}(\text{NMe}_2)_4$ solution ($\text{Ti}(\text{NMe}_2)_4$: 0.021 mmol, 5.0 μL , *n*-hexane: 1.0 mL) was injected into a tube reactor under nitrogen atmosphere. After that, the solvent was removed in a dynamic vacuum (10^{-2} Pa), which was beneficial for the $\text{Ti}(\text{NMe}_2)_4$ sublimation and reacting with the disk. The samples prepared in this way were used for *in-situ* IR technique studies.

2.3.2. The ¹³C CP-MAS NMR spectra

All of the samples were recorded on a Bruker Avance 500 spectrometer equipped with a standard 4 mm double-bearing probe head and operating at 125.73 MHz for ¹³C CP-MAS NMR. The freshly prepared samples were immediately sealed in the 4 mm zirconia rotor in a glove box. Compressed air was used for both bearing and driving the rotors. Chemical shifts are reported in ppm downfield from SiMe_4 (± 0.1 and 1 ppm ¹³C NMR spectra). Samples were introduced under argon in a zirconia rotor, which was then tightly closed.

2.3.3. Catalytic testing

Catalytic activity in benzaldehyde cyanosilylation reaction was evaluated by Gas Chromatography (GC). Benzaldehyde (1.0 mmol) and trimethylsilyl cyanide (1.0 mmol) were added into 20 mL toluene and stirred with 20 mg as-prepared titanium catalysts (2 mol% Ti) for 12 h at room temperature. The conversions of the benzaldehyde and yield of cyanosilylation products were determined by internal standard (GC experiments were performed on an Agilent 7890 A Gas Chromatography).

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