



# Sol-gel preparation of helical silicate containing palladium oxide nanoparticles and the application for nitration of aromatic compound



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## ABSTRACT

Two palladium-containing silicates are prepared through sol-gel, and doping of L-sodium lactate plays a key role for giving helical morphology. The helical silicate is modified by chiral sulfonyl chloride in order to modulate coordination environment of palladium for enhanced catalysis. The porosity, composition, crystalline nature and bulk chirality have been studied too. All synthetic silicates show high yields for nitration of arenes by using available nitro-source. Both solvent acidity and oxidant seem crucial to nitration more than others. The conversion of larger arene is related to catalyst porosity, and modification of silicate with chiral sulfonyl chloride shows varied results. Furthermore, two catalysts exhibit renewable recycling behaviors, proving their interior palladium could be utilized. Lastly, a tetravalent palladium-facilitated mechanism is proposed. This work may contribute to the design and catalytic application of nanosized or micro-sized silica material with particular morphology.

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## 1. Introduction

Nitrocompounds are important building blocks for construction of pharmaceuticals, polymers, dyes, or other fine chemicals [1–3], and meanwhile nitration reactions have been widely studied in synthetic chemistry [4–6]. Traditionally, nitration is carried out by using strongly oxidizing mixed acid (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>) [7] or dinitrogen pentoxide [8]. However, these methods usually suffer from some drawbacks including poor functional group tolerance, low stereoselectivity, and high corrosion as well [9]. Therefore, developing new, efficient, benign and low-cost nitration processes would show great values for both academic and industrial concerns.

In recent years, transition metal-catalyzed nitration of organic compounds has aroused wide attentions. Maiti and co-workers have provided a one-pot method for nitration of arylboronic acid by using bismuth catalyst [10]. Later, the palladium-catalyzed aerobic oxidative nitration of arene is developed by employing *tert*-butyl nitrite as nitro-source [11,12]. Furthermore, the copper-catalyzed tyrosine nitration comes into sight, where copper complex plays as a Fenton reagent in producing nitroxyl radical from nitrite [13].

Additionally, both silver nitrite (AgNO<sub>2</sub>) [14] and ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>) [15] are proved to be efficient catalysts too. On the other hand, zeolite ZSM-5 is introduced to heterogeneous nitration, exhibiting advantages for this transformation [16,17]. Overall, significant progresses have been made in homogeneous area, but there is still a big room for exploring heterogeneous catalyst, expanding scopes of substrate and nitro-source, and optimizing catalytic condition, instrumental or environmental influence as well.

With the successes of zeolites that achieved in oil refinery, silica-based mesoporous materials such as MCM-41 [18] and SBA-15 [19] arouse continuous interests. These materials are usually made from hydrolysis of tetraethoxysilane (TEOS) in sol-gel, using hexadecyltrimethylammonium bromide (C<sub>16</sub>TAB) or polymer (Pluronic P123) as template in favor of material morphology and texture [18,19]. And meanwhile, specialized metal could be incorporated for purpose of catalysis [20]. Furthermore, some properties of silica-based materials like good morphology and porosity, or varied type of doped metal have shown important effects on catalysis [21]. Obviously, developing metal-containing silica materials exhibits great prospects for heterogeneous progress.

It is challenging to prepare micro- or nano-sized silica-based catalyst with particular morphology. For instance, natural chirality is a remarkable phenomenon, easily found in biological substances such as protein and cellulose. However, artificial materials rarely

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show chiral appearance, like helices or asymmetric center [22]. In certain cases, chiral templates may agglomerate into micelles in association with tetraethyl orthosilicate (TEOS) during sol-gel, which sometimes gives chiral morphology of product [23]. Thus, using appropriate templates seems to be a reasonable option for building chiral silica material.

Furthermore, some silica materials featuring chiral morphologies such as helicity would show unique and highly efficient catalytic properties, including chemoselectivity and chiral induction [24,25], which actually mean a lot to the progresses of both homogeneous and heterogeneous catalysis. Therefore, developing helical silica as catalyst may show some positive influences on optimizing traditional nitration.

It is also interesting to study mechanism of nitration. When palladium compounds are used as nitration catalysts, Stahl [26] and Sanford [27] propose that Pd(II) may be oxidized into Pd(IV) species through a single-electron-transfer (SET) procedure, which then adsorbs and activates C–H bond. Also, Liu and co-workers put forward a palladium(II/III) and/or palladium(II/IV) catalytic cycle for nitration of aromatic compounds under oxidizing conditions [28,29]. But in practice, the frequently-used palladium salts are expensive and non-recyclable, the risks of product contamination and cost of catalysis are both rising. In the future, endeavors on heterogenization along with mechanism research should be more important and popular.

This work aims to develop an efficient, benign and recyclable system for nitration of arenes. Bivalent palladium is incorporated into silicate through sol-gel, where special template is also loaded for modulating morphology of sol-gel product. Then, chiral sulfonyl chloride is further attached to material surface in order to give additional coordination to the doped palladium for enhanced catalysis. Various arenes are tested, and catalyst recycling is carried out too. Lastly, a mechanism is proposed based on catalytic results and calculations. This work may contribute to the design of silica material with unique morphology as well as particular catalytic property.

## 2. Experimental

### 2.1. Starting materials

Hexadecyltrimethylammonium bromide (C<sub>16</sub>TAB, 98%), tetraethyl orthosilicate (TEOS, 98%), L-sodium lactate (L-SL, Scheme 1, 99%), ammonia solution (25 wt.%), palladium(II) chloride (59% Pd), L-(–)-10-camphorsulfonyl chloride (L-CSC, 98%), D-(+)-10-camphorsulfonyl chloride (D-CSC, 97%), 3-(methoxycarbonyl)phenylboronic acid (3-Mcpba, 98%, Table 3), ammonium persulfate ((NH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 99%) and trifluoroacetic acid (TFA, 99%, Table 3) are purchased from Accela. The 1,3,5-trimethylbenzene (mesitylene, 97%), ethylbenzene (99.5%), *tert*-butylbenzene (99.5%) and naphthalene (99.7%) are commercially available from Aladdin. Toluene, benzene, acetic acid (ACA, 99%, Table 3) and inorganic salts are provided by local suppliers.

### 2.2. Instruments

Scanning electron microscopy (SEM) is tested on JEOL JSM-6700F at 20.0 kV without Au coating. Transmission electron microscopy (TEM) is tested on JEOL JEM-200CX at 120 kV. Low-angle ( $2\theta = 0.5^\circ - 10^\circ$ ) and wide-angle ( $2\theta = 10^\circ - 80^\circ$ ) X-ray diffractions are collected on Philips X'Pert Pro diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), with interval of  $0.05^\circ \text{ s}^{-1}$ . The static contact angle is measured according to conventional sessile drop method by a charge-coupled device (CCD) camera (Sony XC-ST70CE). X-ray photoelectron spectroscopy (XPS) is carried out on Kratos Axis Ultra DLD, using monochromatic Al K $\alpha$  X-ray

(1486.6 eV) as irradiation source, and the binding energy scale is calibrated by using C 1s peak at 284.8 eV. Background subtraction is performed, and peaks are fitted by employing Gaussian-Lorentz (G/L) product function with 30% Lorentzian.

BET surface area, pore volume, pore radius and pore size distribution are measured on Micromeritics ASAP 2020, using N<sub>2</sub> adsorption isotherms at 77.35 K. Samples are degassed at 150 °C in vacuum before testing. Surface area is calculated using the multi-point Brunauer-Emmett-Teller (BET) method based on adsorption data with relative pressure  $P/P_0$  of 0.06–0.3. Total pore volume is obtained from N<sub>2</sub> adsorbed at  $P/P_0 = 0.97$ . Pore volume and pore radius are determined using Barrett-Joyner-Halenda (BJH) method.

FT-IR is detected in KBr pellets on Bruker Tensor 27, with wave numbers of 400–4000 cm<sup>–1</sup>. Raman spectra are recorded on Horiba HR 800 spectrometer with a charge-coupled device (CCD) camera detector, and the line of 514 nm is derived from Spectra Physics 2018 Argon/Krypton Ion Laser system. UV–vis spectra are measured in dichloromethane on UV1800, Shimadzu. Thermo-gravimetric analysis (TGA) is performed on NETZSH TG 209C featuring TASC 414/4 controller under nitrogen protection, with a heating rate of 10 K/min at 303–1073 K. Differential scanning calorimetry (DSC) is carried out on NETZSH DSC 214 under nitrogen protection, with a heating rate of 10 K/min at 303–573 K.

Bulk chirality of synthetic sample is determined according to the established method [30]. In practice, sample (50 mg) and L-(or D-)valine (20 mg) are added to distilled water (50 mL). The mixture is vigorously stirred at 25 °C for 120 min. Concentration of L-(or D-)valine is measured by using UV spectra at 210 nm (UV 1800, Shimadzu) under sampling at regular intervals. Adsorption percentage is deduced in the light of adsorption value of 20 min according to Lambert-Beer's Law.

GC–MS is tested on GCMS-QP2010 Plus, Shimadzu, with Rxi-5 ms capillary column (length 30 m, internal diameter 0.25 mm). For part of GC, column temperature is 60 °C, injection port temperature is 250 °C, sampling mode is split-flow, split-ratio is 26, carrier gas is helium. For part of MS, ion source temperature is 200 °C, and interface temperature is 250 °C. Palladium content in catalytic solution is measured on inductively coupled plasma atomic emission spectrometry (ICP-AES), ICPE-9000, Shimadzu.

### 2.3. Preparation of palladium-containing helical silicates

In practice, C<sub>16</sub>TAB (0.40 g, 1.09 mmol), palladium (II) chloride (0.08 g, 0.45 mmol) and L-sodium lactate (0 mmol for PdSi0; 0.05 g, 0.43 mmol for PdSi1; Scheme 1) are dissolved in aqueous ammonia (25 wt.%, 100 mL) at 40 °C. TEOS (2.0 mL, 1.86 g, 8.95 mmol) is introduced. The mixture is slowly stirred at 40 °C for 3 h, and then aged at 100 °C for 24 h in autoclave. Brown solids (PdSin,  $n = 0-1$ ) are filtered after being washed with distilled water ( $3 \times 10 \text{ mL}$ ) and absolute ethanol ( $3 \times 10 \text{ mL}$ ), dried in air, then calcined at 550 °C for 5 h to remove templates, yielding PdSi0 (1.50 g) and PdSi1 (1.67 g) as brown powders.

### 2.4. Modification of palladium-containing helical silicate

PdSi1 (1.0 g), L-(or D-)CSC (725 mg, 2.9 mmol) and triethylamine (0.5 mL, 365 mg, 3.6 mmol) are vigorously stirred in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 20 °C for 10 h. After removal of solvent under reduced pressure, the residue (PdSi1R or PdSi1S, Scheme 1) is washed with distilled water ( $3 \times 10 \text{ mL}$ ) and absolute ethanol ( $3 \times 10 \text{ mL}$ ), then dried in air. PdSi1R and PdSi1S are obtained as brown powders with masses of 1.27 g and 1.30 g respectively.

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