Highly Efficient Aerobic Oxidation of Alcohols Using a New Recoverable Catalyst, the Role of Mesoporous Channels of SBA-15 to Stabilize Palladium Nanoparticles

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Experimental Procedures, Physical Data and Transmission Electron Microscope images (TEM) of the Catalysts

Preparation of SBA-15: The synthesis of SBA-15 has been achieved using known procedure described by Stucky and his co-workers (see reference 10b of the manuscript). In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw ≅ 5800) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35 °C. Then 8.50 g of tetraethoxysilane (TEOS) was added into that solution with stirring at 35 °C for 20 h. The mixture was aged at 80 °C overnight without stirring. The solid was filtered off and washed thoroughly with hot ethanol/water using a Soxhelet apparatus for 18 h to remove the surfactant molecules. It was dried in air at 110 °C overnight.
**Preparation of SBA-15 surface bound carboxylic acid:** The preparation of SBA-15 surface bound carboxylic acid was achieved according to the known procedure described by Clark et al. (*Chem. Commun* 1996, 1859 and *Chem. Commun.* 1998, 2707): The resulting SBA-15 (6 g) was allowed to react with 3-cyanopropyltriethoxysilane (2 mmol, 0.462 g, Fluka) in refluxing dry toluene (150 mL) under nitrogen for 24 h. The solid was filtered off and was washed thoroughly with hot toluene and ethanol. It was dried in air at 90 °C overnight to furnish the corresponding surface bound cyanopropyl group at a loading ca. 0.33 mmol g⁻¹ (Determined by elemental analysis). The absorption band at 2256 cm⁻¹ along with bands 2900-3000 cm⁻¹ clearly indicates the attachment of cyanopropyl group onto the surface of SBA-15 (Figure 1). The CN-SBA-15 was hydrolyzed by heating in 50% (v/v) aqueous sulfuric acid at 150 °C for 3h. After cooling to room temperature, the resulting solid was filtered off and filter cake was washed with an excess of deionized water. Drying in an oven at 110 °C overnight furnished the corresponding SBA-15-COOH with approximately the same loading.

![Scheme 1](image)

**Figure 1.** DRIFT-IR of surface-bound Cyanopropyl onto SBA-15
Preparation of palladium complex covalently anchored onto silica (Catalyst 1): The ligand A was first prepared by stirring a mixture of surface-bound carboxylic acid (5 g), 2, 2’-bipyridylamine (1.7 mmol, 0.291 g, Aldrich) and dicyclohexylcarbodiimide (1.7 mmol, 0.350 g, Merck) in dry THF (150 mL) at reflux temperature for 72 h. The solid was filtered off and washed thoroughly with hot ethanol using a Soxhelet apparatus for 18 h to remove both the urea by-products and unreacted starting materials. It was then dried in an oven at 110 ºC overnight to furnish the corresponding surface-bound bipyridyl amide A at a loading ca. 0.2 mmol g⁻¹ (Determined by TGA and elemental analysis, Figure 2). The catalyst was then prepared by stirring a mixture of surface bound ligand A (4 g) and palladium acetate (0.11 mmol, 0.025 g, Merck) in dry acetone (100 mL) at room temperature for 24 h. After stirring the white brown solid was filtered, washed with large volume of acetone, ethanol and ether in order to remove any adsorbed palladium on the surface. It was then dried in an oven at 95 ºC overnight to furnish the corresponding catalyst 1 at a loading ca. 0.022±0.001 mmol g⁻¹ (atomic absorption spectroscopy (AA)).
Further Characterization of the Catalyst: The catalyst 1 was further characterized by atomic absorption spectroscopy (AA), elemental analysis, transmission electron microscopy (TEM) and surface pore analysis. From the AA analysis of 1, it is calculated that the loading of palladium was 0.022±0.001 mmol. g⁻¹. We have used such a low loading in order to minimize the catalyst’s leaching. Typically, a nitrogen adsorption desorption type IV with a very sharp hysteristis loop, which is characteristic of the ordered mesoporous materials, was obtained (Figure 3).

**Figure 2.** TGA/DTA diagram of A
BET surface area 455 m$^2$/g and a total pore volume 0.76 cm$^3$/g were measured for the first sample of the catalyst, respectively. BJH calculations showed an average pore size 76 Å (7.6 nm) for this catalyst, which is in good agreement with the pore diameter estimated by TEM (Figure 3, 4). The TEM images interestingly showed that the nano-architecture of the catalyst (SBA-15 channels) survived even after prolonged refluxing at 150 °C in concentrated sulphuric acid (stage 2, scheme 1).
General experimental procedure for oxidation using molecular oxygen: A mixture of K₂CO₃ (1 mmol) and Catalyst 1 (0.18 g, ~0.4mol% of Pd) in Toluene (5 mL) was prepared in
a two-necked flask. The flask was then evacuated (water aspirator) and refilled with pure oxygen for three times (balloon filled). To this solution the alcohol (1 mmol, in 1 mL toluene) was then injected and the resulting mixture was stirred at 80 °C under an oxygen or air atmosphere (for the indicated time in the Table 1). After completion of the reaction, the reaction mixture was filtered off and the catalyst rinsed twice with CH₂Cl₂ (5 mL) the excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds. A TEM of the catalyst 1 after the oxidation reaction showed that Pd nanoparticles with relatively regular size ca. 7 nm were mostly formed inside the regular mesoporous channels (Figure. 6).

**Figure 6.** TEM image of the recovered catalyst 1 across to the channels, the palladium nanoparticles with a relatively regular size clearly can be seen inside the channels.

The N₂ adsorption analysis of the recovered catalyst showed very similar isotherms to those of the fresh catalyst 1 with relatively sharp adsorption and desorption branches in the \( P/P_0 \)
rang of 0.5-0.8. This strongly indicates a relatively narrow mesopores size distribution even in the recovered catalyst (Figure 7), although the total pore volume decrease from 0.76 to 0.57 cm$^3$ g$^{-1}$. This observation accompanied with the TEM results suggests that most of the nanometer-scaled void space and channels of the host SBA-15 remain open, although a small portion of the channels may be blocked by Pd nanoparticles (Figures 5, 6, supporting information).

**Figure 7.** Isotherm plot of the recovered catalyst

**The results of recovery of the catalyst:**

Recycling experiments were examined for the aerobic oxidation through a set of small-scale experiment (5 mmol scale). Thus, after the first run, which gave the corresponding benzaldehyde in $>99\%$ GC yield (83% isolated yield), after recovery the catalyst was successfully subjected to 12 subsequent aerobic oxidation reaction from which it gave the
benzaldehyde in essentially >99% GC yield (corresponding to a total TON = 3000) with slight changes in reaction time mainly due to the lose of the catalyst during the recovery. We think that the number of reaction cycles, and therefore turn over number (TON) can still be increased upon the increasing of the reaction scale. The results are shown in the following Table 2.

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<th>Entry</th>
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<th>R²</th>
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<th>Yield (%)</th>
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<td>&gt;99</td>
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* GC Yield based on internal standard method unless otherwise stated. *b Yields in parentheses refer to isolated pure products. *c The molar ratios of substrate: 1 are 1:0.004.