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Investigation on the catalytic reduction kinetics of hexavalent chromium by viral-templated palladium nanocatalysts

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ABSTRACT

We report on examination of the dichromate reduction reaction mechanism and synthesis–structure–activity relationship of palladium (Pd) nanoparticles formed on surface-assembled viral templates. By employing Langmuir–Hinshelwood mechanism, the adsorption of formic acid on the catalytic sites is found to be substantially higher (~300 times) than that of dichromate ions. The viral-templated Pd nanocatalysts with optimized synthesis conditions are demonstrated to have higher catalytic activity per unit Pd mass for the dichromate reduction reaction than the commercial Pd/C catalysts. The effects of catalyst synthesis conditions on the catalyst properties (i.e. Pd particle size and loading) and on the catalytic activity are also investigated via Grazing Incidence Small Angle X-ray Scattering (GI-SAXS) and reaction kinetics studies. The changes in our biotemplated nanocatalyst synthesis conditions contribute to the changes in the Pd particle size and surface loading density, leading to predictable manipulation of the catalytic activity. We expect that the new insights on the reaction kinetics and reactant adsorption behavior as well as the catalyst synthesis–structure–activity relationship reported in this work can be readily extended or applied to other catalysts and reaction systems.

1. Introduction

Novel nanocatalysts have been widely applied for the waste water clean-up processes due to the advantages of high reaction efficiency and selectivity, low mas-transfer restrictions, low cost, and environmentally benign procedures [1,2]. Particularly, palladium (Pd) is an important catalyst metal for the hydrogenolysis of organohalogen compounds [3], oxidation of methanol [4], and reduction of heavy metal pollutants [5,6]. Hexavalent chromium (Cr(VI)) is a ubiquitous toxic pollutant in the aquatic environment [7]. Catalytic reduction of hexavalent chromium (Cr(VI)) provides a promising alternative to the existing non-catalytic treatments such as adsorption, biosorption, membrane filtration, ion exchange, and electrochemical treatment [8]. There have been many reports on the catalytic reduction of Cr(VI) with organic reductants by applying oxides [9] (TiO_2 [10], aluminum oxide γ-Al_2O_3 [11], goethite α-FeOOH [12]), nano-sized zero-valent iron [13], nano-sized mixed metallic particles [14], palladium nanoparticles [5,6], mesoporous Al_2O_3-supported [11] or TiO_2-supported [15] Pd nanoparticles. Yet, there exist critical challenges in predictable and readily controllable synthesis of efficient catalysts with sufficient recyclability and reactivity. Furthermore, reaction kinetics study of the Pd catalyzed dichromate reduction by formic acid still remains lacking. In order to further understand and to design optimal reaction conditions and processes for novel catalyst systems, a thorough study on the reaction mechanism as well as on the catalyst synthesis–structure–activity relationship is much needed.

We utilize tobacco mosaic virus (TMV) as a biotemplate for the controlled synthesis of palladium nanocatalysts [16–18]. Specifically, TMV is a plant virus consisting of 2130 identical coat proteins helically encapsulating a 6.4 kb genomic mRNA. As a biologically derived template for nanoparticle synthesis, TMV possesses a range of unique advantages including precisely controlled nanotubular dimensions (300 nm long, 18 nm outer diameter, 4 nm inner channel) and unusually high stability (e.g. pH 2–10, organic solvents, high temperature) as well as safety and simple mass production [19,20]. In addition, there are several advantages of using viruses as biotemplates for the formation of metal nanoparticles in catalysis, including genetic modification for additional functionality [21–23], preferential and size-controllable particle formation [24], catalyst loading density and spatial control [18]. As shown in the schematic

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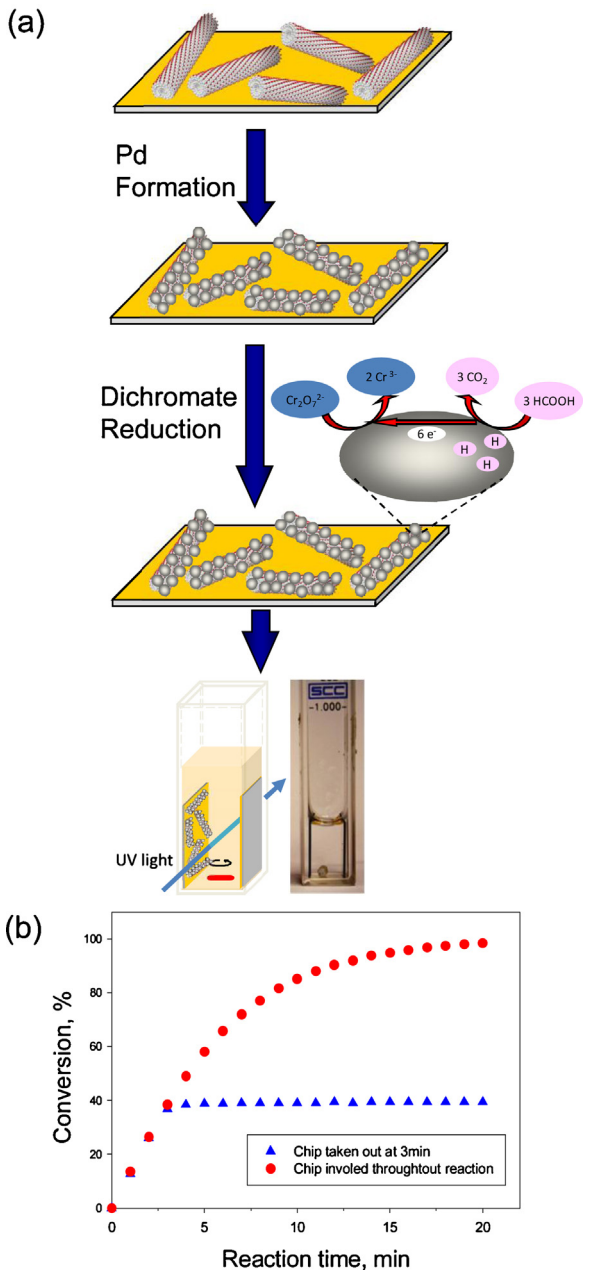

Fig. 1. (a) Schematic diagram depicting the synthesis of TMV-templated Pd nanocatalyst for catalytic dichromate reduction reaction. (b) Confirmation of the surface reaction by chip removal. The TMV-templated Pd catalyst synthesis condition: 0.5 mM Na_2PdCl_4, 15 mM $NaPH_2O_2$, 20 min incubation. The dichromate reaction condition: 0.1 mM $K_2Cr_2O_7$, 100 mM NaCOOH + HCOOH, pH = 3, 25 °C.

diagram of Fig. 1(a), our catalyst synthesis approach involves the surface assembly of TMV on gold-coated silica chips, followed by tunable Pd nanoparticle formation on the TMV templates via chemical reduction of Pd precursors with a mild reducing agent sodium hypophosphite [16,24]. The as-prepared TMV-templated Pd catalyst chips are immersed in a small volume of reaction mixture to carry out the reactions. Such surface-assembled format allows for in situ real time monitoring of the reaction extent, fast screening of reaction conditions, and simple catalyst and product recovery, all of which further make the study of reaction mechanism and kinetics readily feasible.

Exploiting these advantages of viral-templated Pd nanocatalysis, we examined the surface catalyzed reaction mechanism, kinetics and the catalyst synthesis–structure–activity relationship for dichromate reduction in this report. The results indicate: (1) Pd-catalyzed dichromate reduction follows Langmuir–Hinshelwood surface reaction mechanism, and the adsorption of formic acid is found to be significantly higher (~300 times) than that of dichromate ions, (2) our viral-templated Pd nanocatalysts with optimized synthesis condition show 68% higher catalytic activity in comparison with commercially available 5% Pd/C catalysts, and (3) the Pd nanoparticle size, catalyst loading density and catalytic activity of viral-templated Pd nanocatalysts can be readily controlled simply by tuning the chemical compositions (e.g. Pd precursor and reducer concentrations) during the synthesis under mild aqueous conditions. Meanwhile, larger Pd particles were found to show higher catalytic activity per unit Pd surface area, suggesting size-dependent behavior of Pd catalyzed dichromate reduction with formic acid. We envision that these results and the methodologies presented here can be applied to examine other novel catalyst systems and reactions, such as dechlorination reactions involving surface adsorption of multiple reactants [25,26].

2. Materials and methods

2.1. Materials

Gold-coated silicon wafers with 1000 Å Au were purchased from Platypus Technologies (Madison, WI). Sodium tetrachloropalladate(II) (Na_2PdCl_4, 99.998%), $NaPH_2O_2$ (>98%), and Potassium dichromate ($K_2Cr_2O_7$, 99.5%) were purchased from Sigma–Aldrich (St. Louis, MO). Sodium formate (HCOONa, 99%), concentrated hydrochloric acid (HCl, 37%), and nitric acid (HNO_3, 70%) were from Thermo Fisher Scientific Inc. (Waltham, MA). Standard Palladium on carbon (Pd/C, 5%) catalyst was purchased from Alfa Aesar (Ward Hill, MA) and used without further treatment for the dichromate reduction reaction study.

2.2. Synthesis of TMV-templated Pd catalysts

Genetically modified tobacco mosaic virus (TMV1cys) was extracted from infected tobacco leaves by phosphate extraction buffer, followed by chloroform phase separation, and PEG8000 sedimentation. The sucrose gradient technique was applied for the virus purification as previously reported [22]. The synthesis method for the Pd-TMV catalyst chips is similar to our previous report [16] with minor modification. Briefly, clean gold chips were incubated in aqueous 100 μg/mL TMV1cys solution for surface assembly, which yields consistently dense near-monolayer surface coverage. These TMV-assembled chips were then exposed to various Na_2PdCl_4 precursor solutions in the presence of $NaPH_2O_2$ as reducer for 20 min metallization under ambient conditions to form Pd nanoparticles preferentially on the TMV templates [16,17,24,27]. These Pd-TMV chips were then thoroughly rinsed with deionized water, dried, and stored for the reaction and characterization studies.

2.3. Catalytic dichromate reduction

For the dichromate reduction, potassium dichromate was the source of Cr(VI) and formic acid was the electron donor under acidic environment (pH = 3)[16]. The catalytic reactions were carried out in a quartz cuvette with vigorous stirring at 25 °C. The reaction extent was continually monitored by measuring the absorbance at 350 nm with Evolution™ 300 UV/vis spectrophotometer (Thermo Scientific, Waltham, MA). The ionic Equations for the redox reaction are shown in Eqs. (1) and (2) [28].

$$Cr_2O_7^{2-} + 14H_3O^+ + 6e^- \leftrightarrow 2Cr^{3+} + 21H_2O \quad (1)$$