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Lattice distortion induced electronic coupling results in exceptional enhancement in the activity of bimetallic PtMn nanocatalysts

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ABSTRACT

Lattice strain plays a critical role in structural heterogeneity and surface electronic properties of bimetallic nanocatalysts. However, understanding of how to engineer optimal electron transfer in anisotropic bimetallic crystals remains a grand challenge to achieve enhanced catalytic performances. We investigate beyond conventional polymer based core-shell and alloy structures, and present unique lattice distorted PtMn catalysts fabricated *via* a cooperative self-assembly method. The strong internal strain between Pt and Mn lattices is found to induce the structural distortion of anisotropic PtMn crystals and formation of asymmetric flower shapes, leading to stretched Pt and contracted Mn lattices. Such distorted bimetallic crystals exhibit unusual electronic coupling and an *eight-fold* synergistic enhancement in catalytic oxidation of renewable biomass feedstocks compared with monometallic Pt catalysts. The novel synthesis technique and revealed electronic coupling mechanism described herein opens the door for the rational discovery of other bimetallic nanocatalysts with positive synergy.

1. Introduction

The development of novel catalytic materials is a key for resource-efficient technologies for platform chemicals with reduced environmental impact [1–3]. Extensive research has already shown that bimetallic and multimetallic catalysts often exhibit enhanced catalytic performances compared with monometallic ones due to tunable morphology and composition [4,5]. Although these materials can be synthesized with precise control and particle size and tailored structures such as cubic, rhombic and octahedral shapes, they often consist of low indexed facets with limited surface catalytic activities [6–8]. Therefore, the discovery of novel nanomaterials with enhanced anisotropy and tunable electron configuration, which display high surface catalytic activities, has received much attention in recent years [9]. In the area of bimetallic materials, Pt-based nanostructured catalysts have been one of the most extensively studied systems because they not only show exceptional performances in fuel cell and petrochemical upgrading, but also in emerging areas such as biomass conversion and solar cells [10].

In the past decade, major research efforts have been made on fabricating bimetallic Pt-*3d* metal nanomaterials due to their tunable synergy in catalysis [6,11–15]. It is established in classic catalysis theories that atoms on highly indexed sites display superior activities than others. Therefore, conventional strategies on tuning the surface geometries of bimetallic crystals, and thereby to enhance catalytic activity, is by altering the morphologies of Pt-3*d* bimetallic structures through adding ligands [16]. Manipulation of crystal growth kinetics using ligand-metal interaction as the external driving force results in enlargement of surface roughness. This well-known methodology has been established by several research groups and summarized in several reviews [4–10,16,17]. Numerous results have confirmed that PtCo, PtCu, PtNi and PtFe particles with cubic, spherical, truncated octahedral and wired structures can be fabricated by mixing ligands [*e.g.* polyvinylpyrrolidone (PVP)] with metal precursors, in solvents containing polyols or amines [18–21]. For example, a two-step method involving PVP mixed with Cu seeds led to hollow nanocaged or nanoframe structured PtCu particles [22]. Branched PtNi nanostructures are reported using Pt seeds as templates [23,24], while didodecyldimethylammonium bromide stabilized Ni seeds generate PtNi nanodendrites [25].

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Similar techniques have also been employed to synthesize other *3d* metal based nanomaterials [26–32], as well as other bimetallic combination such as PtAu, PtPd, *etc.* [10]. It is clear that two-step ligand directed seed/template growth is the main methodology to create anisotropic high index nanoparticles. Although the ligand-metal force is effective in facilitating anisotropic growth, a major drawback is that such bimetallic crystals often lack strong internal interaction and structural coherence, easily decomposing or deactivating [9,33] when exposed to complex reaction environment [34].

Classic bottom up synthetic methodologies are primarily focused on ligand-mediated surface index for morphologically influenced catalysis (facet dependent catalysis), which can be attributed to activity enhancements of bimetallic nanocatalysts [35]. But recent research in nanomaterials has discovered that electron transfer and metal–metal interfacial strain can intrinsically enhance structural coherence and surface properties of bimetallic crystals [36–38], where extensive studies have shown that rather than forcing two metal species to form bimetallic nanoparticles using polymer stabilizers, lattice strain induced by difference in lattice parameters among the metal species can be used as a driving force to generate unique nanoparticles. Interfacial strain often induce unusual lattice stretch or contraction in bimetallic crystals. Such lattice distortion undoubtedly leads to tunable surface electronic properties and thus affecting catalytic activities of bimetals. This is because that the strong cohesive interaction at metal–metal interface ("ligand" effect) involves charge transfer or rehybridization of electron orbitals of two metals. The perturbation of a metal's orbitals intrinsically shift *d* band towards/away from Fermi level [36]. Therefore, in the area of catalysis, this finding offers a new methodology and provides immense potential for innovative catalyst design [34,35]. Engineering optimal electronic coupling by altering metal–metal interfacial lattice strain and understanding its impact on catalytic activity of bimetallic materials have been attracting extensive attention in recent years [9,36,39].

There are three fundamental aspects which need to be addressed in present work: (a) proposing a ligand-free method for cooperative assembly of exchange coupled bimetallic nanocrystals, (b) investigating the plausible mechanism of lattice distorted and coupled growth of bimetallic crystals and (c) understanding how lattice distortion of crystals influences electronic coupling and surface catalytic properties. Using bimetallic PtMn crystal as a model system, we studied in this paper a polymer free one pot self-assembly method to synthesize exchange coupled nanoclusters. The anisotropic growth is induced by large lattice constant mismatch between the two metals (Pt: *fcc*, 0.39 nm; Mn: *bcc*, 0.89 nm). In this approach, well-controlled *bud- and cauliflower-shaped* PtMn clusters were grown in the absence of polymer stabilizers and immobilized on heterogeneous support (*i.e.* CeO_2) in one pot process. The influence of Pt/Mn ratio, solvent and chemical promoters on the lattice strain of PtMn clusters were systematically studied. Surface morphologies of PtMn catalyst samples were characterized using transmission electron microscopy (TEM), while information on Pt and Mn interaction, surface electronic properties and lattice distortion were obtained from X-ray photoelectron spectroscopy (XPS). A plausible mechanism for lattice distorted anisotropic growth of bimetallic PtMn is discussed. While reported studies on PtMn nanocatalysts deal with reactions involving simple substrates such as methanol [40–43], we investigated the performances of PtMn clusters for catalytic oxidation of renewable biomass-derived feedstocks ($C_{2\text{-}3}$ polyols) in aqueous phase under relatively mild conditions (70 °C, 1 atm O_2).

This work shows that anisotropic growth induced lattice distortion and electronic coupling leads to exceptional (8 fold) enhancement in the activity of bimetallic PtMn nanocatalysts for oxidation of biomass feedstocks. The structure-activity correlation of these catalysts obtained from biomass oxidation results provides guidance for rational design of synergistic bimetallic catalysts for selective activation of C—H and C—O bonds encountered in the processing of renewable fuels and chemicals.

2. Experimental section

2.1. Chemicals

Glycerol, lactic acid, glycolic acid, formic acid and dimethylformide (DMF) were purchased from Sigma Aldrich. Glyceric and tartronic acids were obtained from Fisher Scientific. Metal precursors such as $Pt(acac)_2$ and $Mn(NO_3)_2$ as well CeO_2 powders were also purchased from Sigma Aldrich.

2.2. Catalyst preparation

In a typical catalyst synthesis process, 1.2 g of CeO_2 powders and approximately 10 mL DMF solvent were first mixed at room temperature. Known amounts of Pt and Mn precursors were then charged and further mixed with the slurry till dissolved completely. Another 10 mL DMF was also added to the mixture. After transferring into a 100 mL autoclave, the whole slurry was flushed thrice with N_2 at room temperature. The whole mixture was heated at 200 °C under N_2 atmosphere (~2.2 MPa) for about 12 h before cooling down to room temperature. Catalyst powders from each batch of preparation were washed with ethanol/water (2/1 v/v) and centrifuged several times before drying under vacuum overnight. The catalyst samples were tested for oxidation without any further pretreatment. The details of catalyst preparation method are described as follows:

Catalyst preparation was conducted *via* a simple solvothermal method. A schematic description of the preparation step is presented in Fig. 1. In particular, cerium oxide (CeO_2) supported Pt and PtMn catalysts were synthesized using DMF as a solvent. Unlike two-pot or seeded growth methods, reduction of metal precursors, $Pt(acac)_2$ and $Mn(NO_3)_2 \cdot 4H_2O$, was performed in the presence of CeO_2 powder. In other words, both growth of nanocrystals and simultaneous immobilization on the catalyst support were achieved in one pot. The Pt content on CeO_2 support is 1 wt% for all the catalyst samples (identical Pt precursor concentration in all solution), while the atomic ratios of Pt/Mn (1/x) were varied from 1/0.5 to 1/2 (denoted as $PtMn_x$). In a typical catalyst preparation experiment, approximately 1.2 g catalysts were obtained in 20 mL DMF solution. While the CeO_2 powder and metal precursor solution in DMF are yellowish-white and brownish-yellow respectively, the solid products resulting from the one-pot synthesis are grey, suggesting reduction of metal precursors and immobilization of nanoparticles on the CeO_2 support. In addition, the gas atmosphere in the autoclave is also believed to be important in the formation and continuous growth of bimetallic nanocyrstals. In most cases, N_2 was used as the inert blanket, while the reduction of metal precursors was induced by DMF (a weak reducing agent). In some control experiments, H_2 (a strong reducing agent) was added, while in another case benzoic acid (BA, a template agent) was used as a promoter in the DMF medium (see Table S1 for notation).

2.3. Oxidation tests

The experimental procedure for testing catalyst activity for glycerol oxidation was similar to that described previously [44]. Briefly, about 0.05 g of solid catalyst was added to 25 mL aqueous solution containing glycerol (1.0 g) and NaOH (1.7 g), which was transferred to a 100 mL of three neck flask. The slurry was heated in an oil bath with precise temperature control before heating up to a predetermined reaction temperature. Once the liquid slurry attained the