



Facile synthesis, characterization and catalytic activity of nanoporous supports loaded with monometallic and bimetallic nanoparticles



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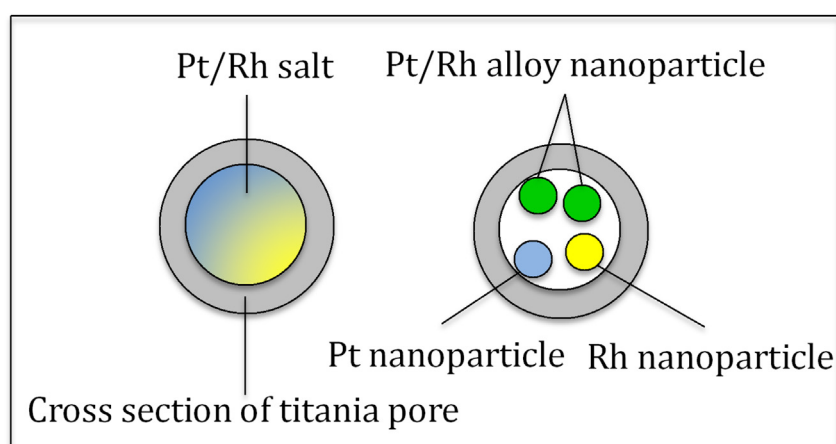
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HIGHLIGHTS

- This paper reports a technique for simultaneously forming a porous support with well-distributed monometallic and alloy catalyst nanoparticles. The catalytic activity for CO oxidation of this titania/platinum/rhodium system is superior to that of a Pt loaded system alone, as well as a commercial catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

When an aqueous platinum chloride or mixed rhodium and platinum chloride solutions are added to a mixture of lecithin, AOT and titanium isopropoxide (TIP) in isooctane, the surfactants partition the aqueous and oil phases into a nanoscale bicontinuous microstructure. Hydrolysis and condensation of the TIP generates a highly connected porous anatase support. Reduction of the metal salt/s in the confined aqueous nanodomains of the bicontinuous template results in monometallic or bimetallic alloy NPs. The NPs are well-distributed throughout the interior surfaces of the support. This route, where monometallic and bimetallic nanoparticles are synthesized together with the support material, can be exploited for generating diverse catalytically active materials for various applications.

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1. Introduction

Nanoparticles supported on metal oxides provide a promising platform [1–3] for fuel cell catalysts [4], photovoltaics [5],

and catalytic converters used in cars. Superior catalytic activity of noble metal nanoparticles (NPs) loaded on active nanoporous metal oxides such as titania has opened new frontiers for research in the field of heterogeneous catalysis [6–9], pertinent to clean energy generation and control of environmental pollution. The intrinsic photocatalytic property of anatase titania coupled with its ability to strongly modify catalytic properties of the metal NPs by metal-support interactions [10] has made it an excellent choice for

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creating catalyst materials. One area where this coupling between support and catalyst nanoparticles has been exploited is CO oxidation, where both rhodium (Rh) and platinum (Pt) NPs have been used as catalysts. Rh NPs show superior catalytic performance for CO oxidation compared to Pt NPs [11]. In mixed systems, synergism between Pt and Rh has been reported [12]. For CO oxidation Pt–Rh bimetallic NPs or mixtures of Pt and Rh nanoparticles have better catalytic activity than Pt NPs alone [13]. Pt–Rh catalysts are also widely used for oxidation of ammonia and in three-way catalysts (TWCs) for suppressing car exhaust emission by NO reduction and CO oxidation [12,14]. Rh serves as the main active component, while Pt prevents deactivation of Rh by poisoning [15]. Bimetallic catalysts have been used in other applications [16,17].

Conventional catalyst-support nanocomposite synthesis techniques such as sol–gel methods [18], impregnation [19], UV irradiation [20] or precipitation from solution [5] rely on the formation of catalyst particles after the creation of support material, often causing a poor distribution of particles inside pores and on the support. These methods also tend to block pores. These factors lead to a reduction in catalyst effectiveness [21].

Here, we present a surfactant-templated synthesis technique for forming well-distributed Pt monometallic and Pt–Rh alloy NPs loaded on a highly patterned and interconnected nanoporous anatase titania support. The alloy, rather than individual nanoparticles, forms when the mixed metal salt is reduced within the highly confined surfactant-mediated template. A uniform distribution of both Pt NPs along with Pt–Rh nanoalloys within the support and the low mass transfer resistance because of the interconnectivity of the pores results in excellent catalytic activity for CO oxidation using these materials.

2. Materials and methods

2.1. Materials

2,2,4-Trimethylpentane (isooctane) (99+%), bis-2-ethylhexyl sulfosuccinate (AOT, 99%), titanium isopropoxide (TIP, 98+%) were obtained from Sigma–Aldrich. Sodium borohydride (NaBH_4 , 99%) L- α phosphatidylcholine (lecithin) were obtained from Acros Chemicals. Anhydrous rhodium (III) chloride (RhCl_3 , 99.9% metals basis) platinum (IV) chloride (PtCl_4 , 99.9% metals basis) are obtained from Alfa Aesar.

2.2. Generation of Pt, Rh loaded titania nanocomposite

AOT (0.8 M) and lecithin (0.4 M) are added to a predetermined volume of isooctane and vortexed at 2500 RPM until a homogeneous, clear yellow gel is formed. TIP in a 1:1 volume ratio to isooctane is mixed into this solution. An aqueous metal salt solution containing 0.015 M PtCl_4 or a mixture of 0.028 M RhCl_3 or a mixture of these salt solutions is prepared. This solution is added to the isooctane/TIP/AOT/lecithin solution to obtain a desired W_o (W_o = Water/AOT molar ratio). A white precipitate is formed immediately due to titania formation. A 0.1 M NaBH_4 solution is then added and the sample vortexed. The sample color changes to black due to reduction of the Pt and Rh salts to their respective metallic states. Excess of NaBH_4 is used to facilitate complete reduction of Pt^{4+} and Rh^{3+} ions. The samples are dried for 24 h at 60 °C, and then calcined by starting at 400 °C and increasing the temperature at half-hour intervals by 50 °C up to 550 °C. The samples are left at 550 °C for 4.5 h. Finally a powder is obtained. The calcination step helps to get rid of traces of surfactants left after solvent removal. Sodium chloride (NaCl) is a byproduct of the reduction reactions between NaBH_4 and Pt, Rh salts. As precipitated NaCl can block the pores and hinder the catalytic performance of nanocom-

posites, samples are washed five times with deionized water after calcination.

2.3. Analytical characterization

A JEOL JEM 2100 transmission electron microscope operating at an accelerating voltage of 200 KV is used to examine the particles. The powdered particles are embedded in an epoxy resin, cured, and 70–90 nm slices are cut using a diamond knife. (MT2-B DuPont Ultramicrotome). Energy dispersive X-ray analysis for elemental analysis was undertaken with an Oxford Inca system. For characterization of nanoparticle dispersion and support structure a Hitachi S-4800 field emission scanning electron microscope is used.

2.4. Catalyst activity

The catalytic activity of the samples is analyzed for steady state CO to CO_2 conversion using a fixed bed reactor (eight-channel reactor, Celero). 0.05 g of a sample is loaded in a 3 mm reaction well. A gas mixture comprising of 1100 ppm CO, 5% O_2 , with the rest being N_2 , is delivered via mass flow controllers at a GHSV of $300,000 \text{ h}^{-1}$. Preheated gases are made to contact the catalyst bed. Once steady state is achieved, the product gases are analyzed using a gas chromatograph equipped with a methanizer and field ionization detector (Shimadzu GC-17A). CO/ CO_2 ratios in the inlet and product streams are used to calculate the conversion efficiency of samples. The catalytic efficiency of samples are compared with commercial catalyst XT25376 obtained from St. Gobain-Norpro, wet impregnated with 1.8% Pt.

3. Results and discussion

Fig. 1a shows a SEM micrograph of the highly organized porous network of TiO_2 supports prepared at $W_o = 70$. The macropores have a diameter ranging from 100–200 nm. Fig. 1b is a higher magnification image showing the presence of mesopores within the macropore walls. These images indicate that TiO_2 inherits the structure of the underlying bicontinuous template. A longitudinal view of the pore topography of the titania support shows a highly interconnected porous network, as indicated in Fig. 1c. Increasing the water content from $W_o = 70$ to $W_o = 200$ increases the macropore diameter (Fig. 1d) [22].

Addition of aqueous solutions of PtCl_4 , RhCl_3 during synthesis of nanocomposites followed by subsequent reduction by sodium borohydride solution yields very well dispersed metal nanoparticles on the pore surfaces of support. The excellent distribution of catalyst NPs in our samples is attributed to uniform distribution of Pt^{4+} and Rh^{3+} ions throughout the aqueous nanochannels of the viscous gel phase. Fig. 2a shows SEM micrographs of a Pt, Rh loaded TiO_2 nanocomposite, with a Pt and Rh loading of 0.9% each prepared at $W_o = 100$. There is a uniform distribution of metal NPs inside the macropores, shown by arrows in Fig. 2b. The particle size is in the range of 2–5 nm. The underlying support morphology is preserved, indicating that salt reduction does not disrupt pore organization [22,23].

A thin-section transmission electron microscope (TEM) image shown in Fig. 3a reveals highly organized pores with diameter ~ 100 nm for $W_o = 70$. It is also evident that TiO_2 essentially inherits the hexagonally patterned morphology of surfactant template. Metal NPs of size ranging from 2 to 5 nm are distributed uniformly around the surface of macropore walls as shown by arrows in the higher magnification TEM image in Fig. 3b.

A high resolution TEM (HRTEM) image (Fig. 4) shows the crystal lattice of metal NPs. The insets in Fig. 4a and b show the Pt (1 1 1) lattice planes having an interplanar distance of 2.265 Å along with ordered lattices fringes of Rh (1 1 1) [2.196 Å], Rh (2 0 0) [1.90 Å]

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