



# Synthesis of supported bimetallic nanoparticles with controlled size and composition distributions for active site elucidation



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## ABSTRACT

Elucidation of active sites in supported bimetallic catalysts is complicated by the high level of dispersity in the nanoparticle size and composition that is inherent in conventional methods of catalyst preparation. We present a synthesis strategy that leads to highly dispersed, bimetallic nanoparticles with uniform particle size and composition by means of controlled surface reactions. We demonstrate the synthesis of three systems, RhMo, PtMo, and RhRe, consisting of a highly reducible metal with an oxophilic promoter. These catalysts are characterized by FTIR, CO chemisorption, STEM/EDS, TPR, and XAS analysis. The catalytic properties of these bimetallic nanoparticles were probed for the selective CO hydrogenolysis of (hydroxymethyl)tetrahydropyran to produce 1,6 hexanediol. Based on the characterization results and reactivity trends, the active sites in the hydrogenolysis reaction are identified to be small ensembles of the more noble metal (Rh, Pt) adjacent to highly reduced moieties of the more oxophilic metal (Mo, Re).

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## 1. Introduction

Haldor Topsøe shared the firm belief that a key to success in the development of new catalytic processes was elucidation of fundamental principles that control catalytic activity, selectivity, and stability [1]. Moreover, an essential component of his vision for catalysis research was characterization of the catalyst, preferably with the catalyst under controlled conditions, and most preferably with the catalyst under reaction conditions. This approach then provides structure–property relations that guide predictions as to how the catalytic properties can be improved by changes in catalyst structure.

Most catalyst characterization techniques provide information about the bulk material or all of the surface sites in the sample simultaneously. For example, a bimetallic catalyst may be comprised of metallic nanoparticles having a wide distribution of metal compositions. In this case, the results from catalyst characterization techniques (such as X-ray absorption spectroscopy (XAS),

X-ray diffraction, elemental analysis, and others) will reflect the contributions from all of the bimetallic compositions in the sample, whereas the observed catalytic properties may be dominated by contributions from a small subset of the bimetallic nanoparticles near a specific composition. Thus, the structure–property relations derived from studies of such catalysts may be misleading. Accordingly, an enabling approach to pursue the research vision championed by Haldor Topsøe is to develop catalyst synthesis methods that produce catalytic materials with a narrow distribution of compositions and structures.

Bimetallic nanoparticles are an important class of materials, offering enhanced properties that surpass their monometallic parent materials due to synergistic effects [2–5]. Bimetallic catalysts have also been identified as promising candidates for a myriad of reactions involved in biomass conversion [6–8]. Various materials synthesis protocols have been explored in the literature to prepare bimetallic catalysts with well-defined nanoparticle size and composition. For example, the Barbier research group pioneered an approach to obtain bimetallic catalysts that uses surface redox reactions to obtain metal–metal interactions in a liquid solvent [9]. They demonstrated this methodology for the synthesis of var-

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ious bimetallic couples, including PtSn [10], PtRe [11], and PtAu [12] catalysts. The Regalbuto group employed strong electrostatic adsorption (SEA) to synthesize supported metal catalysts with well-dispersed single-metal particles, especially at high metal loadings [13]. They also demonstrated synthesis of PtCo and PdCo multimetallic particles by means of sequential SEA and selectively adsorbing cationic ammine complexes of Pd or Pt onto cobalt oxide particles on the carbon support, rendering a strong interaction between a promoter and the catalytic material. Depending on the reduction temperature, the authors obtained homogeneous alloys (high-temperature reduction) or core-shell structures (low-temperature reduction) [14]. The Monnier group employed an electrodeless deposition (ED) procedure that permits controlled deposition of a second metal onto the surface of a pre-existing metallic surface. They demonstrated the preparation of an array of bimetallic catalysts employing the ED method, such as AuPd, PtPd, CoPt, AgPd, and CuPd supported over different supports [15–20]. The Xia research group employed heterogeneous seeded growth to obtain bimetallic nanocrystals, including core-shell bimetallic nanocrystals for PdAu [21], AuAg [22], and PdAg [23]. Recently, atomic layer deposition (ALD), which is a variation of chemical vapor deposition (CVD) and involves a series of self-limiting reactions between precursor vapors and the surface to deposit thin films, has been developed to obtain bimetallic nanoparticles with controlled particle size, composition, and structure. ALD has been used to demonstrate the synthesis of PtPd, RuPt, and RuPd alloys [5,24].

In the present work, we employ the use of “controlled surface reactions” to produce bimetallic catalysts with narrow distributions of particle size and composition for selective hydrogenolysis reactions of biomass-derived oxygenated hydrocarbons. In our previous work [25,26], we identified a promising class of bimetallic catalysts for selective hydrogenolysis reactions, consisting of the combination of a highly reducible metal (e.g., Rh, Pt) with an oxophilic metal (e.g., Re, Mo). Our results are consistent with the findings of the Tomishige research group for hydrogenolysis reactions, where they showed that introduction of Re in a Rh/SiO<sub>2</sub> catalyst has a significant effect on the selectivity of the chemoselective hydrogenolysis of tetrahydrofurfuryl alcohol, tetrahydrofuran, and tetrahydropyran-1-methanol to their corresponding terminal diols [27]. The increased activity and selectivity of the bimetallic catalysts are attributed to the formation of new bifunctional sites that are created by the addition of the oxophilic metal promoter [25,26]. The promotional effect of oxophilic promoters, such as Re, Mo, and W by modification of Rh/SiO<sub>2</sub> catalyst [28,29], was also demonstrated for glycerol hydrogenolysis.

Understanding the nature of the active sites for conventional synthesis methods employed to prepare bimetallic catalysts can be complicated by the poly-dispersity of the samples. The target of the present work is to produce bimetallic catalysts with controlled particle size and composition for RhMo and PtMo catalyst systems to more clearly elucidate the nature of the active sites. Additionally, in less detail, a RhRe system is examined to probe the effect of different oxophilic promoters (Re and Mo) on a specific reducible metal (Rh), in addition to probing the effect of different reducible metals (Rh and Pt) for a specific oxophilic promoter (Mo). It should be noted that even though we refer to our synthesized catalysts as “bimetallic catalysts,” we do not intend to mean that both component metals exist in a zero-valent state. In fact, depending on the type of promoter, the oxophilic component can exist from a fully reduced to a partially oxidized state. For instance, with RhRe/C catalysts, both Rh and Re were found in EXAFS analysis to be fully reduced after reduction in H<sub>2</sub> at 363 K [26]. However, as will be discussed later in detail, for PtMo/C catalysts, Mo was observed to be coordinated to a light scatterer (C/O) suggesting an incomplete reduction of Mo in the bimetallic nanoparticles.

Additionally, it should be noted that we use of term “alloying” not to indicate uniform ordering of constituent metals in the bulk as well as on the surface of the nanoparticles as it is defined in metallurgy, but instead, we intend to suggest bond formation and an intimate contact between the constituent metal atoms, as has been common practice in the recent literature on bimetallic catalysts.

The catalyst synthesis starts with a supported Rh or Pt catalyst, and it involves the selective adsorption and reaction on the reduced metal surface of cyclopentadienyl rhenium tricarbonyl ((C<sub>5</sub>H<sub>5</sub>)Re(CO)<sub>3</sub>) or cycloheptatriene molybdenum tricarbonyl ((C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub>) (typical chemical vapor deposition precursors) dissolved in *n*-pentane in a N<sub>2</sub> atmosphere, followed by solvent removal and a subsequent temperature-programmed reduction in H<sub>2</sub> to achieve alloy formation. We then use scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) to determine the metal particle size and composition distributions of individual nanoparticles, and we compare the average composition of the nanoparticles measured by STEM/EDS with the bulk composition measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). In addition, we employ *in situ* XAS to probe the coordination environment of the oxophilic promoter (Mo) and the reducible catalytic metal (Pt) in PtMo/C. We then carry out reaction kinetics measurements for the selective hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran (HMTHP) to elucidate the effect of the bimetallic composition on catalytic activity.

## 2. Methods and materials

### 2.1. Catalyst synthesis

#### 2.1.1. Controlled synthesis (CS) procedure

For the RhMo/C catalyst, Vulcan XC-72 (Cabot) carbon, RhCl<sub>3</sub> (Mitsubishi Chemical Company, 40% Rh), cycloheptatriene molybdenum tricarbonyl ((C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub>) (Strem Chemicals), *n*-pentane (Sigma-Aldrich), and tetrahydropyran-2-methanol (HMTHP) (Sigma-Aldrich, 98%) were used without further purification. The (C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub> compound and *n*-pentane were stored and handled inside a glove box filled with N<sub>2</sub> atmosphere. As an initial step, a batch of Rh/C parent catalyst was prepared by incipient wetness impregnation (IWI) of the carbon support with an aqueous solution of RhCl<sub>3</sub> to obtain 4.5 wt% Rh loading. The impregnated catalyst was dried at 383 K for 3 h, and then reduced under flowing H<sub>2</sub> at 723 K using a ramp of 0.5 K min<sup>-1</sup>. Subsequently, the Rh/C catalyst was passivated at room temperature with 1% O<sub>2</sub> in He. Portions of this batch were used to prepare a series of RhMo/C bimetallic catalysts with varying Mo content while keeping the same Rh loading. The schematic of the overall synthesis procedure is presented in Fig. 1.

In a typical synthesis, for the addition of Mo, 1 g of the Rh/C parent catalyst was re-reduced under flowing H<sub>2</sub> at 673 K using a ramp of 8 K min<sup>-1</sup> in a Schlenk tube, which was then sealed under H<sub>2</sub> atmosphere after cooling to room temperature (Step 1). Next, in step 2, the (C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub> compound was dissolved in *n*-pentane to yield an orange-red solution, which was contacted with the parent catalyst after unsealing the Schlenk tube inside a glove box under N<sub>2</sub> atmosphere. The slurry was then stirred until the orange-red solution turned clear, suggesting a complete uptake of the precursor from the solution by adsorption onto the catalyst. The uptake of the precursor by the Rh/C parent catalyst was evaluated with FTIR and UV-vis spectroscopy, which is discussed in the following section. The residual *n*-pentane was evaporated under Ar atmosphere using Schlenk techniques. The dried Rh/C catalyst with adsorbed Mo-compound was then subjected to reduction under H<sub>2</sub> flow to a temperature of 773 K (Step 3). The reduced bimetallic

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