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).

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 various 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 employed an electroless 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/SiO₂ 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 is

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/SiO₂ 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 H₂ 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 ((C₅H₅)Re(CO)₃) or cycloheptatriene molybdenum tricarbonyl ((C₇H₈)Mo(CO)₃) (typical chemical vapor deposition precursors) in a N₂ atmosphere, followed by temperature programmed reduction in H₂ 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 XC72 (Cabot) carbon, RhCl₃ (Mitsubishi Chemical Company, 40% Rh), Cycloheptatriene molybdenum tricarbonyl ((C₇H₈)Mo(CO)₃) (Strem Chemicals), *n*-pentane (Sigma-Aldrich) and tetrahydropyran-2-methanol (HMTHP) (Sigma Aldrich, 98%) were used without further purification. The (C₇H₈)Mo(CO)₃ compound and *n*-pentane were stored and handled inside a glove box filled with N₂ 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 RhCl₃ to obtain 4.5 wt% Rh loading. The impregnated catalyst was dried at 383 K for 3 hours, and then reduced under flowing H₂ at 723 K using a ramp of 0.5 K min⁻¹. Subsequently, the Rh/C catalyst was passivated at room temperature with 1% O₂ 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.

Fig. 1. Schematic representation of the controlled synthesis (CS) approach for a RhMo bimetallic catalyst.

In a typical synthesis, for the addition of Mo, 1 g of the Rh/C parent catalyst was re-reduced under flowing H_2 at 673 K using a ramp of 8 K min^{-1} in a Schlenk tube, which was then sealed under H_2 atmosphere after cooling to room temperature (Step 1). Next, in step 2, the $(\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_3$ 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_2 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_2 flow to a temperature of 773 K (Step 3). The reduced bimetallic RhMo/C catalyst was then passivated with 1% O_2 in He. Steps 2 and 3 were repeated to achieve higher Mo loadings (i.e., multi-cycle syntheses). In these multi-cycle syntheses, the bimetallic catalysts were passivated in O_2 only after the final cycle.

As will be discussed, this synthesis technique provides flexibility to add precursor in small excess of the amount that can be fully taken up from the solution. The excess precursor that has not been selectively adsorbed by the parent material during the suspension gets evenly distributed onto the support during the *n*-pentane evaporation. The synthesized catalysts are designated as: *Synthesis Method-Metal1Metal2/Support- Catalyst ID*. The controlled synthesis is abbreviated as CS. The catalysts were also prepared by incipient wetness impregnation (IWI).

The synthesis of the PtMo system was identical to that of RhMo system, except for the preparation of the parent catalyst, which is Pt/C for this system. A batch of Pt/C parent catalyst was prepared by incipient wetness impregnation (IWI) of the carbon support with an aqueous solution of chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) (Sigma Aldrich) to obtain 3.5 wt% Pt loading. The impregnated catalyst was dried at 383 K for 3 hours, and then reduced under flowing H_2 at 533 K using a ramp of 0.5 K min^{-1} . Subsequently, the Pt/C was passivated at room temperature with 1% O_2 in He. The addition of Mo was performed in a similar fashion as for the RhMo system.

For the synthesis of the RhRe/C bimetallic catalysts, the parent Rh/C was similar to that used for the RhMo system. The addition of the Re component was also performed in a similar manner as the other two bimetallic systems, except for the use of the $(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_3$ precursor (Strem Chemicals), which is available in the form of white crystals. Similar to the Mo-precursor, the Re-precursor is completely soluble in *n*-pentane. However, unlike the organometallic Mo precursor, which results in an orange-red solution, the Re precursor yields a clear solution. The amount of precursor adsorption by Rh/C was thus monitored by UV-Vis spectroscopy.

2.1.2 Incipient wetness impregnation (IWI1 and IWI2) procedures

Bimetallic catalysts were also prepared by conventional incipient wetness impregnation (IWI) of the carbon (Vulcan XC-72) support. In the first method (IWI1), the catalysts were prepared by successive impregnation with the component metal salt solutions with intermediate drying at 383 K but without an

intermediate reduction in H₂. The IWI1 catalysts were subjected to a final reduction in H₂ flow at 773 K, followed by a passivation step in 1% O₂ in He. In the second variation (IWI2), a parent Rh/C or Pt/C was first prepared by the reduction of the impregnated salt (RhCl₃ or H₂PtCl₆.6H₂O, respectively) in flowing H₂, similar to the treatment employed in the CS method. In the second step, either an aqueous solution of (NH₄)₆Mo₇O₂₄ salt (Sigma Aldrich) or perrhenic acid (50-54% Re, Strem Chemicals) was impregnated onto the passivated parent catalyst, followed by reduction in H₂ at 773 K. In all cases, the loading of the reducible component (Rh or Pt) was kept constant, while the amount of the oxophilic promoter was varied to obtain a series of bimetallic catalysts of varying composition for comparison with the CS catalysts.

2.2 Reactivity measurements

The reaction chosen to probe the reactivity of the bimetallic catalysts was the hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran (HMTHP) to produce 1,6-hexanediol, an example of an important class of reactions for the production of value added α,ω -diols (Scheme 1).

Scheme 1. Ring opening reaction of 2-(hydroxymethyl)tetrahydropyran (HMTHP).

The reaction kinetics studies were performed in a 50 mL batch reactor (Hastelloy C-276, Model 4792, Parr instrument). Prior to the reaction, the reactor was purged with He and then H₂, and pressurized to 40 bar with H₂. The catalyst was reduced at 473 K with H₂, and then cooled to room temperature. A 5 wt% HMTHP feed solution (25 mL) in milli-Q water (18 M Ω) was injected into the reactor using an HPLC pump. The reaction was executed at 393 K under continuous magnetic stirring. The reactions were performed using a specific amount of catalyst (100-400 mg) and for a specific period of time (4-17 hours) to achieve similar conversion levels. The catalytic performance in different reactions was compared by measuring rates per gram of catalyst ($\mu\text{mol g}_{\text{catalyst}}^{-1}\text{min}^{-1}$) as well as by calculating turnover frequencies

(min^{-1} , sites obtained by measuring CO uptake). The post-reaction mixture was filtered by 2 μm syringe filters and injected into the HPLC for quantitative analysis. The HPLC (Waters 2695) is equipped with a differential refractometer (Waters 410), a photodiode array detector (Waters 996) and an Aminex HPX-87P column (Biorad) maintained at 358 K. A mobile phase of pH 7 milliQ-water at a flow rate of 0.6 mL min^{-1} was used for the analysis.

2.3 Sample Characterization

2.3.1 Inductively Coupled Plasma-Absorption Emission Spectroscopy (ICP-AES)

Metal analyses were performed using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (Perkin-Elmer Plasma 400 ICP Emission Spectrometer). Catalyst samples (~20 mg) were digested in 5 mL of Aqua Regia heated to 423 K below a water-cooled reflux column. Cooled post-digestion solutions were then filtered and centrifuged to remove fine, suspended particles.

2.3.2 CO Chemisorption

The CO adsorption studies were performed using a Micromeritics ASAP2020C apparatus. Prior to measurement of the CO adsorption uptake at 303 K, the catalysts were reduced in flowing H_2 at 473 K for 4 h. For calculation of the exposed noble metal on the surface, a 0.75 ML coverage of CO was assumed at full saturation [25], and this stoichiometry was assumed for simplicity to remain constant upon addition of the promoter.

2.3.3 Temperature Programmed Reduction (TPR)

Temperature Programmed Reduction (TPR) of the Rh/C parent catalyst with adsorbed $(\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_3$ compound was performed using a tube furnace with heating controlled by a PID temperature controller (Love Controls) connected to a K-type thermocouple (Omega). Catalyst (400 mg) was added to a fritted quartz tube and purged with He before beginning reduction. Gas flow was switched to 3% H_2/He at 35 $\text{cm}^3(\text{STP}) \text{min}^{-1}$, followed by initiation of a 10 K min^{-1} temperature ramp. An OmniStar

Gas Analyzer (Pfeiffer Vacuum, Model GST 320) was used to analyze the gaseous effluent. Traces of O₂ and moisture in He were removed by using an O₂ trap.

2.3.4 Fourier transform infrared spectroscopy (FTIR)

2.3.4.1 Solution FTIR

A Nicolet 6700 (Thermo Scientific) Fourier Transform Infrared Spectrometer (FTIR) was used to collect IR spectra of solutions of the organometallic (C₇H₈)Mo(CO)₃ compound. A transmission FTIR cell was used with salt windows and a path length of about 0.5 cm. Approximately 6 mL of precursor solution was added to the cell using a glass pipette, and the cell was sealed with a rubber stopper before setting in front of the IR beam. The cell was washed twice with excess *n*-pentane between sampling. The spectrum of *n*-pentane was used as a reference.

Solutions of (C₇H₈)Mo(CO)₃ in *n*-pentane were prepared in a N₂ atmosphere glove box. Before mixing with dry catalyst, a portion of the precursor solution was kept aside for later analysis. Pre and post-mixed precursor solutions were transported out of a glove box in sealed glass vials. Post-mix solutions required filtration through a 0.2 μm syringe filter to remove residual catalyst solid abstracted during separation in the glove box. Typical pre-mix concentrations of 0.1 wt% (C₇H₈)Mo(CO)₃ in *n*-pentane were bright red-orange in color, turning light orange to clear upon mixing with catalysts, and required 10x dilutions for FTIR to avoid total absorbance of the beam.

2.3.4.2 DRIFTS-FTIR

DRIFTS-FTIR studies were performed with a Rh/silica (Davisil Silica, Sigma Aldrich) catalyst that had been contacted with (C₇H₈)Mo(CO)₃ and then treated in flowing H₂. In addition, FTIR spectra were collected for CO adsorbed on the Rh/silica catalyst with and without deposition of Mo using (C₇H₈)Mo(CO)₃. For DRIFTS studies, a Nicolet 6700 (Thermo Scientific) Fourier Transform Infrared Spectrometer (FTIR) was modified with a Praying MantisTM diffuse reflection accessory, a high temperature-low pressure reaction chamber, and a temperature controller (Harrick Scientific Products).

RhMo/SiO₂ samples with Rh:Mo ratios of 1:0.1 and 1:0.3 were prepared by the controlled synthesis (CS) procedure without the final reduction step. After contacting with (C₇H₈)Mo(CO)₃ in the glove box and evaporation of *n*-pentane in the Schlenk line, the as-synthesized catalysts were placed in the glove box. Under N₂ atmosphere, a powder mixture was prepared containing 10 wt% catalyst in α -alumina which was reduced under flowing hydrogen at 773 K. The powder was mixed, ground, and loaded in the DRIFTS cell. The cell was sealed under N₂ atmosphere and was then mounted in the FTIR spectrometer. An initial spectrum was taken at 298 K under 2% H₂ in Ar at a flow rate of 165 cm³ (STP) min⁻¹. Spectra were taken after heating the cell to 848 K and cooling to 298 K.

Additionally, CO adsorption was monitored by DRIFTS-IR for Rh/SiO₂ and for RhMo/SiO₂ samples with Rh:Mo=0.1 and Rh:Mo=1:0.3. These samples were reduced *in situ* at 673 K under flowing 2% H₂ in Ar. The gas was switched to inert (Ar/He) at 673 K. After purging the sample with inert at 673 K, the cell was cooled to 298 K. An initial spectrum was taken at 298 K under an inert gas flow. Then the sample was dosed with CO for 20 min. After CO adsorption, the sample was purged with inert and a final spectrum was obtained. Traces of O₂ and moisture in He were removed by means of a purifier (Alltech Oxy-Purge N).

2.3.5 UV-visible spectroscopy

A Beckman DU 520 General Purpose UV/vis spectrophotometer was used to collect UV spectra of the (C₅H₅)Re(CO)₃ precursor solution in *n*-pentane. Solutions of (C₅H₅)Re(CO)₃ in *n*-pentane were prepared in a N₂ atmosphere glove box. Pre-mix concentrations of (C₅H₅)Re(CO)₃ were clear to the eye, but required 10x dilution for UV-vis. The spectrum of *n*-pentane was used as a background. Liquid precursor solutions were filled into a quartz cuvette and UV scans were collected in the wavelength range of 190 nm to 240 nm. The amount of the precursor uptake was estimated by the reduction in the peak intensity at 206 nm compared to the absorbance of the initial 0.1 wt% (C₅H₅)Re(CO)₃ precursor solution in *n*-pentane.

2.3.6 Scanning transmission electron microscopy/energy dispersive X-ray spectroscopy (STEM/EDS)

Scanning transmission electron microscopy (STEM) was carried out using a FEI Titan STEM with Cs probe aberration corrector operated at 200 kV with spatial resolution < 0.1 nm. Images were recorded in high-angle annular dark-field (HAADF) mode, with HAADF detector angle ranging from 54 to 270 mrad, probe convergence angle of 24.5 mrad, and probe current of ~ 25 pA. The energy-dispersive X-ray spectroscopy (EDS) results were obtained at the same microscope with convergence angle of 24.5 mrad and beam current of 640 pA, with spatial resolution 0.5 nm. Samples were reduced in a Schlenk tube under H_2 flow at 723 K, cooled to room temperature, sealed in H_2 atmosphere, and then unsealed in a glove box under N_2 atmosphere to avoid contact with air. In N_2 atmosphere, the samples were suspended in ethanol and deposited on carbon-coated copper grids. This sample preparation procedure was found to be important to obtain reliable results. It was observed that the oxidised oxophilic components (Re/Mo) could be leached into solution during the ethanol suspension process. STEM samples were plasma cleaned for 20 min before loading into the microscope.

2.3.7 X-ray absorption spectroscopy (XAS) analysis

XAS measurements were acquired on the insertion device and bending magnet beam lines of the Materials Research Collaborative Access Team (10 ID and 10 BM, MRCAT) at the Advanced Photon Source, Argonne National Laboratory. Measurements were made in transmission in quick scan mode (3 min 30 sec) at the ID line and in step scan mode at the BM line from 250 eV before the edge to 1000 eV beyond the edge. The ionization chambers were optimized for the maximum current with linear response ($\sim 10^{10}$ photons detected sec^{-1}) with 10% absorption in the incident ion chamber and 70% absorption in the transmission detector. A Mo foil (edge energy 20.000 keV) or Pt foil (11.564 keV) spectrum were acquired simultaneously with each measurement for energy calibration.

Reference compounds (MoO_3 , Na_2MoO_4 , $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$, MoO_2 , $Mo_2(CH_3CO_2)_4$ and $C_5H_5Mo(CO)_3$) were ground and diluted with SiO_2 and pressed into self-supporting wafers. Catalysts

were treated in a continuous-flow reactor, which consisted of a quartz tube (1 inch OD, 10 inch length) sealed with Kapton windows by two Ultra-Torr fittings. Ball valves were welded to each Ultra-Torr fitting and served as the gas inlet and outlet. An internal K type thermocouple (Omega) was placed against the catalyst sample holder to monitor temperature. Catalyst samples were pressed into a cylindrical sample holder consisting of six wells, forming a self-supporting wafer. The catalyst amount used was calculated to give an absorbance (μx) of approximately 1.0. The catalysts were treated at 473 K in 3% H_2/He for 1h, purged with He and cooled to room temperature before obtaining the spectra. Traces of O_2 and moisture in He were removed by means of a purifier (Matheson PUR-Gas Triple Purifier Cartridge).

The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point in the leading edge, i.e., the maximum in the first derivative of the leading edge of the XANES spectrum. Experimental phase shift and back scattering amplitude functions were obtained from reference compounds (Mo_2C with 9 Mo-C at 2.10 Å and 12 Mo-Mo at 2.97 Å, Na_2MoO_4 with 4 Mo-O at 1.77 Å, Mo foil with 12 Mo-Mo at 2.76 Å and Pt foil with 12 Pt-Pt at 2.77 Å). Pt-Mo and Mo-Pt phase and amplitude functions were calculated from a scattering pair using FEFF6. The S_0 and $\Delta\sigma^2$ fit parameters were determined by fitting the Pt and Mo foils, respectively. Standard procedures for normalization and background subtraction were performed using WinXAS 3.2 software. The coordination parameters were obtained by a least square fit in R-space of the nearest neighbor, k^2 -weighted Fourier transform data.

3. Results

3.1 Development of synthesis protocol for controlled synthesis (CS) approach

3.1.1 RhMo system

As shown schematically in Fig. 1, the CS method involves synthesizing a Rh/C monometallic parent catalyst as a first step. Next, this Rh/C is re-reduced in hydrogen at 673 K, and without passivating,

it is exposed to a solution containing a pre-determined amount of the $(C_7H_8)Mo(CO)_3$ precursor. The uptake of the precursor by a suspended solid can be monitored visually by the change in color from orange-red to clear. We determined that a precursor concentration sufficient to provide an atomic ratio of Rh:Mo = 1:0.1 (CS-RhMo/C-4, Table 1) can be completely adsorbed by the parent Rh/C catalyst, leaving behind a clear solution in nearly 2 min of suspension. To obtain a quantitative measure of the Mo-precursor uptake, FTIR analysis of the liquid solution before and after suspension was performed. Fig. 2(a) shows the carbonyl stretching spectra for $(C_7H_8)Mo(CO)_3$ in *n*-pentane. Major bands are located at 1997, 1933, and 1909 cm^{-1} , with lower magnitude bands at 1989 and 1880 cm^{-1} . This spectrum compares favorably to the bands at 1984, 1915, and 1887 cm^{-1} observed by Timmers and Wacholtz [30] for $(C_7H_8)Mo(CO)_3$ in methanol. Upon mixing a 0.1 wt% $(C_7H_8)Mo(CO)_3$ in *n*-pentane in a 100:1 solution: solid ratio with blank carbon support (also treated under H_2 at 673 K for consistency), only a 20% decrease in band intensities is observed after 1 h of mixing (Fig. 2(a)). If re-reduced 4.5 wt% Rh/C parent catalyst is mixed with the solution instead, the bands intensities decrease by >99% in a few minutes yielding a clear solution, indicating an almost complete uptake of the Mo-precursor at these concentrations by the reduced Rh metal in the parent catalyst.

For FTIR analysis of the adsorbed CO as well as for the TPR analysis, supported bimetallic catalysts were prepared using a silica (Davisil, Sigma Aldrich) support. The reduction in the band intensity after suspension of blank silica (also treated under H_2 at 673 K) in a 0.1 wt% $(C_7H_8)Mo(CO)_3$ solution in a 100:1 solution: solid ratio was found to be 64% after one hour of mixing, while the uptake for Rh/silica was almost complete (~99%) in few minutes. These spectra again indicate a preferential uptake by the supported metal as compared to the adsorption on the support itself, although the difference was less significant than on carbon, indicating an important role of the support in synthesizing nanoparticles with controlled composition.

To evaluate the effectiveness of a passivated parent material in the uptake of the $(C_7H_8)Mo(CO)_3$ precursor from solution and to investigate the need to re-reduce batches of parent catalysts, synthesis were

also performed with passivated Rh/C parent material (denoted as RhO_x/C). Fig. 2(a) also presents the FTIR analysis of the liquid precursor solution after contacting with Rh/C versus RhO_x/C. While the decrease in the band intensities for re-reduced Rh/C was 99%, the decrease was only 84% with RhO_x/C, indicating that a re-reduced Rh/C parent material more effectively adsorbs the (C₇H₈)Mo(CO)₃ precursor from solution because the reduced metal more effectively binds to the precursor than does the RhO_x. Thus, re-reduction of the parent Rh/C was adopted as a standard step in the CS synthesis protocol.

To further investigate the extent of precursor concentrations that can be taken up by the parent material, syntheses were performed by progressively increasing the concentration of the (C₇H₈)Mo(CO)₃ precursor in the solution. When the concentration was increased to obtain the atomic ratio of Rh:Mo= 1:0.15 (CS-RhMo/C-5), the post suspension solution also became entirely clear, but only after suspending the solid for about 1 h. When the concentration was further increased to obtain Rh:Mo= 1:0.3 (CS-RhMo/C-11) and to 1:0.6 (CS-RhMo/C-12), the residual precursor solution did not become clear after prolonged suspension for several hours. Fig. 2(b,c) shows FTIR analysis of the liquid solutions with varying precursor concentrations. It can be seen from the figure that for Rh:Mo= 1:0.15 (CS-RhMo/C-5) sample, 99% of the precursor was adsorbed by the 4.5 wt% Rh/C parent catalyst. However, for Rh:Mo= 1:0.3 (CS-RhMo/C-11) and for Rh:Mo= 1:0.6 (CS-RhMo/C-12), only 63% and 25%, respectively, of the precursor was taken up by the solution after prolonged suspension steps.

In the light of these observations, to obtain higher Mo contents (atomic ratios Rh:Mo= 1:0.2 and beyond), catalysts were prepared in multiple cycles, with intermittent reductions, to maintain the homogeneity of the synthesis. When the synthesis was performed in multiple cycles of (C₇H₈)Mo(CO)₃ addition, with each cycle depositing enough molybdenum to yield a Rh:Mo= 1:0.15, we found that almost all of the precursor could be taken up by catalyst in each cycle, such that the final solution was clear. As can be seen from Fig. 2(d), the precursor from the solution after the additional cycle in the multi-cycle synthesis is also around 99% adsorbed by the RhMo/C parent material from the first cycle.

While the higher loadings were achieved in multiple cycles, for comparison, three catalysts with the atomic ratio of Rh:Mo= 1:0.2 (CS-RhMo/C-10) , 1:0.3 (CS-RhMo/C-11) and 1:0.6 (CS-RhMo/C-12) were also prepared in a single cycle. In these syntheses, the excess precursor gets distributed onto the support after the solution is removed by evaporation. During the final reduction step in H₂, this excess precursor may become mobile (M.P. = 374 K) and can potentially decompose onto the reduced Rh metal forming Rh-Mo bonds to form bimetallic nanoparticles with higher Mo content. To evaluate whether that was actually the case, characterization studies of these single step CS catalysts were also performed, and the results for these catalysts are presented for comparison in Table 1.

Fig. 2. FTIR spectra of the $(C_7H_8)Mo(CO)_3$ solution in *n*-pentane before and after suspension of (a) C, Rh/C, and RhO_x/C, (b) Rh/C for Rh:Mo= 1:0.3 (CS-RhMo/C-11) in a single cycle, (c) Rh/C for Rh:Mo= 1:0.6 (CS-RhMo/C-12) in a single cycle, (d) catalysts in subsequent cycles.

In addition to the determination of the uptake of $(C_7H_8)Mo(CO)_3$ from the solution, we also studied the decomposition of the adsorbed precursor that takes place during the final reduction step using TPR and FTIR analysis. Fig. 3 presents the TPR profiles of various decomposition species. Three main decomposition species that were tracked using the MS detector are CH_4 (fragment CH_3 , $m/z=15$), CO ($m/z=28$) and CO_2 ($m/z=44$).

Fig. 3. TPR profiles of various species evolved as a result of the decomposition of $(C_7H_8)Mo(CO)_3$ precursor adsorbed on a re-reduced Rh/SiO_2 ($Rh:Mo= 1:0.15$).

It can be seen from the TPR profiles that CH_4 evolution as a result of the decomposition of the cycloheptatriene ligand commenced at a temperature around 410 K. The CH_4 peak attained maxima at 534 K and at 670 K, while the CO evolution began around 730 K, reaching a maximum around 850 K. Additionally, we also observed evolution of CO_2 along with CO , a species probably formed as a result of disproportionation reactions. Since the peak height in CO TPR profile was observed to be maximum at 850 K, the same temperature was also used in the FTIR analysis. Fig. 4 shows the difference in FTIR spectra of the $Rh:Mo= 1:0.3$ sample before and after treatment in hydrogen at 850 K, demonstrating the loss of C-H and C-O stretching frequencies for the ligands of the adsorbed $(C_7H_8)Mo(CO)_3$ precursor

upon treatment at elevated temperature. The loss of surface hydroxyl groups is also observed in the spectrum.

Fig. 4. Difference in FTIR spectra before and after H_2 treatment showing decomposition products from heating $(C_7H_8)Mo(CO)_3$ precursor adsorbed on a re-reduced Rh/SiO_2 ($Rh:Mo = 1:0.3$).

Accordingly, both FTIR and TPR studies confirm the decomposition of the $(C_7H_8)Mo(CO)_3$ precursor during the final reduction step of the synthesis. The CS synthesis protocol that we employed involved a reduction step in which the catalyst containing the $(C_7H_8)Mo(CO)_3$ precursor was heated to 773 K in hydrogen, followed by a 1 h hold to accomplish the removal of ligand and formation of Rh-Mo bonds.

3.1.2 PtMo and RhRe systems

As mentioned in Section 2.1.1, for the PtMo system, a Pt/C parent catalyst was synthesized and used with the same $(C_7H_8)Mo(CO)_3$ precursor that was used for the deposition of Mo. It was noted for the PtMo system that the change in the color of the precursor solution from orange-red to clear was slower compared to the RhMo system for the same Pt:Mo composition of 1:0.1. This difference is due to a lower number of total metal sites for similar loadings on the weight basis due to a higher atomic weight of Pt as

compared to Rh. Importantly, however, the color of the Mo-precursor solution for the composition Pt:Mo= 1:0.15 (CS-PtMo/C-1) also turned clear after approximately 1 h of contact with the parent Pt/C catalyst. Accordingly, this composition was used in multiple cycles to obtain the bimetallic catalysts with higher Mo content. Additionally, single cycle catalysts for comparison were also prepared to obtain higher Mo contents.

For the RhRe system, a similar Rh/C parent catalyst was used as for the RhMo system. A re-reduced Rh/C parent catalyst was suspended in a solution of the $(C_5H_5)Re(CO)_3$ solution for 1 h. Subsequently, the solution was removed by evaporation on a Schlenk line. The analysis of the precursor solution using UV-vis spectroscopy is presented in Fig. 5. For the $(C_5H_5)Re(CO)_3$ solutions, the maximum absorbance was observed around 206 nm. The decrease in peak height for the solution after suspending the blank carbon support for one hour was around 14%, whereas the decrease was around 41% for Rh/C catalyst. This result indicates preferential adsorption of the precursor onto the metal as compared to the support itself. However, the controlled surface reaction of $(C_5H_5)Re(CO)_3$ on Rh does not appear to be as favorable as that for the $(C_7H_8)Mo(CO)_3$ precursor. This experiment illustrates the importance of the choice of precursor in the CS approach, and it is necessary to determine the preferential uptake to successfully synthesize uniform bimetallic nanoparticles via this CS approach.

Fig. 5. UV-vis spectra of the 0.1 wt% $(C_5H_5)Re(CO)_3$ precursor solution in *n*-pentane before and after suspending blank C versus Rh/C in a 100:1 solution:solid ratio to achieve Rh:Re = 1:0.15. The solutions were diluted 10x in *n*-pentane.

Because of a partial uptake of the $(C_5H_5)Re(CO)_3$ precursor from the solution (Fig. 5) by the parent catalyst, the excess $(C_5H_5)Re(CO)_3$ precursor remained in solution. Similar to the RhMo system, this excess precursor becomes distributed over the catalyst during the evaporation step, which during the final reduction step in H_2 may become mobile (M.P. = 380 - 384 K) [31] and can potentially decompose onto the reduced Rh metal, forming Rh-Re bonds to form bimetallic nanoparticles. Consequently, all RhRe catalysts were prepared in a single cycle.

3.2 Characterization results

3.2.1 RhMo System

3.2.1.1 Chemisorption and FTIR analysis

Characterization results for the synthesized bimetallic RhMo/C catalysts are summarized in Table 1. For the parent Rh/C catalyst, the CO uptake was $226.7 \mu\text{mol g}^{-1}$. The CO uptake decreased to around $187 \mu\text{mol g}^{-1}$ (an 18% reduction) after molybdenum addition for samples with an atomic ratio of Rh:Mo in the range 1:0.01 to 1:0.1. The CO uptake was further decreased to around $165 \mu\text{mol g}^{-1}$ for the ratio 1:0.15 (CS-RhMo/C-5) (a 23% reduction), to around $133 \mu\text{mol g}^{-1}$ (a 41% reduction) for 1:0.2 (CS-RhMo/C-10), to around $109 \mu\text{mol g}^{-1}$ (a 53% reduction) for 1:0.3 (CS-RhMo/C-11) and to around $80 \mu\text{mol g}^{-1}$ (a 63% reduction) for 1:0.6 (CS-RhMo/C-12). It should be noted that all of these syntheses were performed in a single cycle under similar conditions except for the amount of Mo. It should also be noted that the CO uptakes were similar for the Rh:Mo= 1:0.15 catalysts prepared using a single cycle or in two cycles (Table 1) (CS-RhMo/C-5 and CS-RhMo/C-6). These observations suggest that initial decrease in the 1st cycle (226.7 to $187 \mu\text{mol g}^{-1}$, 18%) is due primarily to sintering. Specifically, the uptake was lower after the 1st cycle (around $140 \mu\text{mol g}^{-1}$) than for monometallic Rh/C ($226.7 \mu\text{mol g}^{-1}$), but it stayed nearly constant with an increase in Mo loading for the composition range of Rh:Mo =

1:0.01 to 1:0.1, and it decreased further only for Mo loadings higher than 1:0.15. In subsequent cycles, the further decrease in CO uptake is primarily due to the decrease in surface coverage of exposed Rh atoms with increasing coverage by Mo atoms. We believe that a major reason for this initial decrease due to sintering is the rapid ramp rate of 10 K min⁻¹ rather than a slower rate of 0.5 K min⁻¹, which is used for the synthesis of monometallic Rh/C or Pt/C. Since the sintering in subsequent cycles was not significant (Table 1, Rh:Mo = 1:0.15, CS-RhMo/C-5 and CS-RhMo/C-6), the fast ramp rate was adopted to shorten the synthesis time.

The aforementioned continuous trend of decrease in the CO uptake suggests an increasing surface coverage of Mo on the Rh nanoparticles with increasing Mo content, which causes a decrease in the number of exposed Rh atoms available for CO chemisorption. For the 1:0.45 (CS-RhMo/C-8) and 1:0.6 (CS-RhMo/C-9) catalysts prepared in three and four cycles respectively, the decrease in the CO uptake was 62% and 75% respectively. A comparison of CS catalysts with similar composition of 1:0.6, but either prepared in a single cycle (CS-RhMo/C-12) or in 4 cycles (CS-RhMo/C-9), shows in Table 1 that the decrease in CO coverage is more significant for the multicycle CS catalyst. We believe this behavior is primarily due to more selective coverage of nanoparticles with Mo atoms in the multi-cycle synthesis. This will be discussed in detail with STEM/EDS results in the next section. This observation is consistent with the selective adsorption of the organometallic precursor by supported Rh, which leads to the formation of bimetallic nanoparticles, possibly in such a way that the Mo atoms remain on the nanoparticle surface.

Table 1. RhMo characterization results.

Catalyst ID	Details	At. Rh:Mo (Theo.)	At. Rh:Mo (ICP)	Rh wt% (ICP)	Mo wt% (ICP)	At. Rh:Mo (EDS)	Rh sites ($\mu\text{mol g}^{-1}$) ^a
Rh/C	Parent catalyst by WI	1:0	-	4.50	0	N/A	226.7
CS-RhMo/C-1	CS - 1 cycle	1:0.025	1:0.01	4.70	0.05	-	193.2

CS-RhMo/C-2	CS - 1 cycle	1:0.05	1:0.03	4.50	0.11	-	185.6
CS-RhMo/C-3	CS - 1 cycle	1:0.075	1:0.06	4.59	0.26	-	194.3
CS-RhMo/C-4	CS - 1 cycle	1:0.1	1:0.11	4.10	0.42	1:0.10	186.9
CS-RhMo/C-5	CS - 1 cycle	1:0.15	1:0.16	4.50	0.67	-	165.3
CS-RhMo/C-6	CS - 2 cycles	1:0.15	1:0.15	4.35	0.61	1:0.17	174.7
CS-RhMo/C-7	CS - 3 cycles	1:0.3	1:0.28	4.50	1.17	1:0.25	134.9
CS-RhMo/C-8	CS - 3 cycles	1:0.45	1:0.40	4.42	1.65	-	86.9
CS-RhMo/C-9	CS - 4 cycles	1:0.6	1:0.45	4.32	1.82	1:0.24	56.4
CS-RhMo/C-10	CS - 1 cycle	1:0.2	1:0.15	2.81	0.44	1:0.17	133.2
CS-RhMo/C-11	CS - 1 cycle	1:0.3	1:0.30	3.16	0.79	1:0.26	108.9
CS-RhMo/C-12	CS - 1 cycle	1:0.6	1:0.67	3.60	2.30	1:0.28	82.7

^a assuming 0.75 ML coverage of CO at full saturation [25]

Fig. 6 shows the FTIR spectra of the samples after CO adsorption. For the Rh/SiO₂, the major band at 2060 cm⁻¹ corresponds to linearly bonded Rh-CO. The bands at 2100 and 2035 cm⁻¹ are attributed to symmetric and anti-symmetric geminals of Rh-(CO)₂. The band at 1884 cm⁻¹ corresponds to the bridge-bonded Rh₂CO. It is clear from these spectra that the addition of Mo to the Rh/SiO₂ catalyst leads to the selective loss of bridge-bond CO, indicating Mo is present on the surface of the Rh nanoparticles, resulting in a decrease in the size of the Rh-ensembles on the surface. In addition, Mo appears to interact with the highly dispersed Rh species associated with the silica support that are responsible for the formation of dicarbonyl species. The decrease in the overall intensity of the FTIR bands for adsorbed CO as the amount of Mo in the sample increases is also consistent with the CO chemisorption results.

Fig. 6. FTIR spectra of adsorbed CO on Rh/SiO₂ and RhMo/SiO₂.

3.2.1.2 Bimetallic composition analysis

Analyses of 30 to 50 individual particles were carried out by STEM/EDS measurements to probe the distribution of bimetallic particle compositions. The average particle composition is presented in Table 1. The overall composition determined by ICP is also presented in the table. For catalysts prepared by controlled synthesis (CS) with a Rh:Mo atomic ratio up to 1:0.3 (prepared in up to three cycles), there is good agreement between the composition values determined by EDS and ICP. These results provide evidence that the CS strategy produces a high level of homogeneity in the synthesis of bimetallic catalysts. However, it can be seen from Table 1 that for syntheses to obtain a higher Mo content beyond Rh:Mo= 1:0.3, the synthesis in 3 cycles (to obtain Rh:Mo= 1:0.45 (CS-RhMo/C-8)), and in 4 cycles (to obtain Rh:Mo= 1:0.6 (CS-RhMo/C-9)), did not result in a complete uptake of the organometallic precursor, as indicated by a mismatch between the theoretical and ICP values. We suspect that this loss of Mo is due to the deposition of the precursor onto the Schlenk glass walls. Moreover, the STEM/EDS analysis of the CS catalyst prepared by depositing 4 cycles of Mo indicated disagreement between the ICP and EDS values. This observation indicates that there is a limit to the amount of Mo that can be deposited and alloyed with the CS technique. With an increase in the amount of Mo in the RhMo

bimetallic nanoparticles, the proportion of surface Mo increases, as evidenced by a decrease in the extent of CO adsorption. Since the adsorption from the later cycles remains incomplete, it indicates that the interaction of the cluster with a surface Mo is not favorable. Additionally, since the overall Mo loading (ICP) on the catalyst prepared in 4 cycles was higher than that of the catalyst prepared in 3 cycles while the EDS-determined composition in the particles remained the same, it appears that Mo deposited in the 4th cycle was primarily on the support rather than on the bimetallic nanoparticles.

Fig. 7 presents composition distribution plots for comparison of catalysts prepared by controlled synthesis and by incipient wetness impregnation methods. For comparison, vertical lines in the plots also indicate the ICP values. Fig. 7(a) compares RhMo/C catalyst with Rh:Mo= 1:0.3. The CS catalyst (CS-RhMo/C-7) displayed the narrowest distribution and was centred at the ICP bulk composition value, signifying homogeneity of the system. The IWI1 catalyst also displayed a bell-shaped curve; however, the distribution was broader. The IWI2 catalyst, which was prepared in two steps (i.e., reducing the first metal before adding the second metal, as in to the CS method), displayed the broadest distribution with a greater number of monometallic Rh nanoparticles, which suggests a large percentage of particles with segregated metals. In Fig. 7(b), the compositions of four different catalysts are presented; all prepared using the CS approach. A narrow bell-shaped distribution is observed for the three first catalysts (CS-RhMo/C-4, CS-RhMo/C-6, CS-RhMo/C-7), centred at the composition value that matches the ICP values. This behaviour demonstrates the compositional homogeneity of the catalysts prepared by the CS technique. Note that there is a slight displacement of the composition distribution with respect to the ICP value on the catalyst prepared by deposition of 3 cycles (CS-RhMo/C-7). Additionally, as discussed earlier, it can be seen clearly that the catalyst prepared by deposition of 4 cycles (CS-RhMo/C-9) presents a similar distribution to that of the catalyst prepared in 3 cycles (CS-RhMo/C-7). Fig. 7(c) presents catalysts with three different compositions (same Rh content and varying Mo content) prepared by the IWI1 technique. These catalysts showed broad composition distributions. For the ratio Rh:Mo= 1:0.1, many of the nanoparticles were determined to be monometallic Rh nanoparticles, and for the same sample

there were many other particles with compositions that were greater than the overall composition determined by ICP. These bimetallic nanoparticles with Mo content higher than the ICP value, along with the finely dispersed Mo species on the support, account for the mismatch between the ICP and the number averaged composition value if the nanoparticles determined by EDS. A similar scenario of broad compositions, with Mo at% lower and higher than the ICP value, along with the presence of Mo species on the support could be seen from Fig. 7(c) for other ratios as well. Fig. 7(d) presents two catalysts with different compositions prepared using the IWI2 technique. It appears that this technique resulted in the broadest composition distribution of the three techniques.

Fig. 7. EDS-determined composition distributions of RhMo/C catalysts: (a) comparison of CS (CS-RhMo/C-7), IWI1, and IWI2 catalysts for a bimetallic composition of Rh:Mo= 1:0.3, (b) CS catalysts with four different bimetallic compositions (CS-RhMo/C-4, CS-RhMo/C-6, CS-RhMo/C-7, CS-RhMo/C-9), (c) IWI1 catalysts with three different bimetallic compositions, (d) IWI2 catalysts with two different bimetallic compositions. X-axis= Mo atomic%, Y-axis= number of particles, vertical lines in the plots

indicate the ICP-AES values. Rh:Mo ratios in the legends are the theoretical values based on the amount of Mo present in the organic solution.

For further evaluation of the CS approach, several higher Mo content catalysts, with compositions varying from 1:0.1 to 1:0.6, were also prepared in a single step. As mentioned above, a portion of the precursor is adsorbed onto the metal nanoparticles during the suspension step, while the excess precursor becomes finely distributed onto the support upon solvent evaporation. All these catalysts undergo final reduction in hydrogen (TPR step) and the compositions were evaluated using EDS analysis of individual particles. It can be seen from Table 1 that while uniformity could be maintained in terms of particle composition for the atomic ratio of Rh:Mo= 1:0.2 (CS-RhMo/C-10) and to a significant extent also for 1:0.3 (CS-RhMo/C-11), it cannot be maintained for 1:0.6 (CS-RhMo/C-12), where the high residual amount of the Mo precursor leads to non-uniformity due to the deposition of finely dispersed Mo on the support or in form of larger Mo aggregates not considered in the EDS analysis.

Fig. 8 presents particle size distributions for each catalyst prepared by the CS technique obtained by acquiring STEM images and measuring particle diameters using ImageJ software. As mentioned in the previous section, it can be seen in Fig. 8 (a-b) that after the first Mo-addition cycle, the average particle sizes for the catalysts prepared by the CS technique are larger than that of the parent monometallic catalyst. It can also be seen from Fig. 8 (c-e) that, for subsequent cycles of Mo-addition, the increase in the particle size is not as significant as for the first cycle. For the subsequent cycles, the sintering was not significant and the increase in the particle size is likely due to the growth in the particles as more Mo is added (Table 1). This observation is consistent with CO chemisorption results, where there was an initial decrease in uptake after the first cycle, even though the amount of Mo added was low, whereas the decrease in the CO uptake in multi-cycle catalysts with higher Mo content was mainly due to the higher surface coverage of the nanoparticles with Mo atoms.

Fig. 8. Particles size distribution for (a) Rh/C and (b-e) RhMo/C catalysts: (b) 1 cycle (CS-RhMo/C-4), (c) 2 cycles (CS-RhMo/C-6), (d) 3 cycles (CS-RhMo/C-7) and (e) 4 cycles (CS-RhMo/C-9). The errors reported are the standard deviation of the mean.

3.2.2 PtMo System

3.2.2.1 Chemisorption and STEM analysis

Characterization results for the various PtMo/C catalysts synthesized by the CS technique are summarized in Table 2. For the 3.5 wt% monometallic Pt/C catalyst, a CO uptake of $117.3 \mu\text{mol g}^{-1}$ was

measured. For CS catalysts, similar to the RhMo system, there was an initial decrease in the CO uptake to around 66 $\mu\text{mol g}^{-1}$ (a 43% reduction) after the synthesis step to add up to 0.5 wt% Mo (Pt:Mo= 1:0.3 (CS-PtMo/C-2)). Further increase in the Mo content to obtain an atomic ratio of Pt:Mo= 1:0.5 (CS-PtMo/C-3) in three cycles, resulted only in a slight incremental decreases in the CO uptake (49% reduction). A CS catalyst prepared to obtain an atomic ratio Pt:Mo= 1:0.6 (CS-PtMo/C-4) in a single step resulted in similar uptake as other CS catalysts with lower Mo content. Thus, it can be concluded that, after the initial reduction in CO uptake (partially attributed to sintering), neither additional cycles, nor increased Mo loading, result in a significant further decrease in the CO uptake, possibly because reduction of the resultant catalyst does not appear to yield a completely metallic nanoparticle (see section 3.2.2.2).

Table 2. *PtMo characterization results.*

Catalyst ID	Details	At. Pt:Mo (Theo.)	At. Pt:Mo (ICP)	Pt wt% (ICP)	Mo wt% (ICP)	At. Pt:Mo (EDS)	Pt sites ($\mu\text{mol g}^{-1}$) ^a
Pt/C	Parent catalyst by WI	1:0	-	-	-	-	117.3
CS-PtMo/C-1	CS - 1 cycle	1:0.15	1:0.18	3.28	0.29	1:0.08*	66.0
CS-PtMo/C-2	CS - 2 cycles	1:0.3	1:0.31	3.24	0.49	1:0.16	70.9
CS-PtMo/C-3	CS - 3 cycles	1:0.45	1:0.48	3.13	0.73	1:0.46	60.9
CS-PtMo/C-4	CS - 1 cycle	1:0.6	1:0.60	3.19	0.93	1:0.28	59.2

* 30% of the particles are pure Pt, ^a assuming 0.75 ML coverage of CO at full saturation [25]

EDS analyses of individual bimetallic nanoparticles were performed for selected PtMo/C catalysts by considering around 30 particles for the analysis in each case. For comparison, CS catalysts Pt:Mo= 1:0.48 (prepared in 3 cycles) (CS-PtMo/C-3) and 1:0.6 (prepared in a single cycle) (CS-PtMo/C-4) were analyzed using EDS (Fig. 9). An apparent difference between these two catalysts, however, was that the

distribution for the single cycle catalyst was skewed towards lower Mo content as compared to the corresponding ICP value. The number averaged EDS values for bimetallic compositions for these two catalysts are presented in Table 2. It can be seen that there is good agreement between the ICP and the EDS value for the 3 cycle catalyst (CS-PtMo/C-3); however, for the single cycle catalyst (CS-PtMo/C-4), the actual composition of Mo in the particles is lower (a number averaged bimetallic composition of Pt:Mo= 1:0.28) than the overall composition, indicating that a significant percentage of Mo went onto the support. In addition, the low loading Mo catalysts (CS-PtMo/C-1 and CS-PtMo/C-2) also show less Mo by STEM/EDS than by ICP. This difference between the RhMo and PtMo systems might be caused by the lower molar loading of Pt compared to Rh on the carbon support, leading to the availability of a higher concentration of defects sites on the carbon to which the Mo-precursor might be bonded, again highlighting the importance of the role of the support. After these defect sites become populated with Mo, then the deposition of Mo in the subsequent cycles becomes more selective for addition to the metal nanoparticles. This would explain the fact that in general, the CS PtMo/C catalysts tended to have a composition distribution slightly displaced to lower Mo content compared to the corresponding ICP value, with the catalyst prepared in 3 cycles having a distribution that is closest to the ICP value.

Fig. 9. EDS-determined composition distributions of PtMo/C catalysts prepared by 1 and 3 cycles of Mo deposition. X-axis= Mo atomic%, Y-axis= number of particles, vertical lines in the plots indicate the ICP-AES values. Pt:Mo ratios in the legends are the theoretical values based on the amount of Mo present in the organic solution.

3.2.2.2 XAS analysis

To better understand the structure of the bimetallic nanoparticles we performed XAS on the PtMo/C CS and WI catalysts. Obtaining quantitative fits of the samples was complicated by the presence of a light scatterer located around 2.05-2.12 Å. This distance is too short for metal-metal scattering and significantly longer than typical Mo=O scattering that would be present in unreduced Mo. One origin for this behavior is incomplete reduction of the Mo (which is fully oxidized Mo(VI) when scanned in air before pretreatment) when reducing the PtMo bimetallic particles at mild conditions (473 K). Evidence of Mo-O or Mo-OH single bonds at a distance of 1.98 Å has been reported previously [32], and we can obtain reasonable fits to the experimental data (Table 3 for Pt L_{III} edge and Table 4 for Mo K edge) by using a Mo-O bond at a distance of 2.06 Å.

Table 3. EXAFS fits for the Pt L_{III} edge assuming molybdenum oxide.

Sample	Description	Scatterer	N	R (Å)	$\sigma^2 \times 10^3$ (Å ²)	E ₀ (eV)
CS-PtMo/C-1	CS 1 cycle	Pt-Pt	8.1	2.71	2	-4.7
		Pt-Mo	1.8	2.69	2	12.1
CS-PtMo/C-2	CS 2 cycle	Pt-Pt	7.8	2.71	2	-5.0
		Pt-Mo	2.0	2.69	2	11.2
CS-PtMo/C-3	CS 3 cycle	Pt-Pt	7.3	2.71	2	-5.3
		Pt-Mo	2.1	2.69	2	11.2
IWI1-PtMo/C-1	0.4% Mo	Pt-Pt	9.8	2.74	2	-2.4
		Pt-Mo	1.5	2.69	2	8.3
IWI1-PtMo/C-2	0.8% Mo	Pt-Pt	8.8	2.74	2	-2.2
		Pt-Mo	1.7	2.69	2	7.5
IWI1-PtMo/C-3	1.3% Mo	Pt-Pt	8.6	2.74	2	-2.6
		Pt-Mo	1.8	2.69	2	6.9

The estimated uncertainties are: N, ±20%; R, ±0.02 Å

Table 4. EXAFS fits for the Mo K edge assuming molybdenum oxide.

Sample	Description	Scatterer	N	R (Å)	$\sigma^2 \times 10^3$ (Å ²)	E ₀ (eV)
CS-PtMo/C-1	CS 1 cycle	Mo-O	1.0	2.06	2	-3.0
		Mo-Pt	3.2	2.69	2	-8.4
CS-PtMo/C-2	CS 2 cycle	Mo-O	1.3	2.06	2	-3.2
		Mo-Pt	2.2	2.69	2	-10.3
CS-PtMo/C-3	CS 3 cycle	Mo-O	1.6	2.06	2	-3.4
		Mo-Pt	1.6	2.69	2	-12.3
IWI1-PtMo/C-1	0.4% Mo	Mo-O	1.3	2.06	2	-2.9
		Mo-Pt	2.5	2.69	2	-11.3
IWI1-PtMo/C-2	0.8% Mo	Mo-O	1.6	2.06	2	-2.4
		Mo-Pt	1.8	2.69	2	-13.5
IWI1-PtMo/C-3	1.3% Mo	Mo-O	1.7	2.06	2	-2.3
		Mo-Pt	1.8	2.69	2	-14.4

The estimated uncertainties are: N , $\pm 20\%$; R , ± 0.02 Å

In addition, we can fit the XANES of the bimetallic nanoparticles using a linear combination of Mo foil and MoO₂. However, we note that the edge energy of the samples is in agreement with that of Mo-C in Mo₂C (20.0018 keV). Thus, we also examined the possibility that the scattering due to the light element was caused by Mo-C rather than Mo-O. In this case, the fit bond length of the light scatterer matches well with the bond length of Mo₂C (2.10 angstroms, Table 5 and 6), providing additional evidence that carbide may have been formed. We note that the whereas the oxide model was the anticipated structure from physical intuition, the carbide model was able to fit the experimental data with less perturbation to known bond lengths, and the Mo₂C XANES aligned well with the sample XANES. In light of these fits, we are not prepared to suggest one structure in favor of the other at this point. In fact, the inability to irrefutably distinguish between the carbide and oxide may suggest that a mixed molybdenum-carbide-oxide phase has been created, which has been observed before under similar conditions [33].

Fortunately, regardless of the exact identification of the light scatterer in the PtMo/C catalysts, several important trends emerge from analysis of the EXAFS data in Tables 3-6. First, the total scattering

around Pt is always less for the CS catalysts than the WI catalysts, indicating that despite the slight sintering that may occur, the CS synthesis leads to smaller average particles. Next, for both the CS and WI catalysts, as the Mo loading increases, the Pt-Mo scattering increases while the Mo-Pt scattering decreases. This trend suggests that as Mo loading increases, only a fraction of it will come in contact with Pt atoms (increasing Pt-Mo, the number of Mo scatterers around a Pt atom) while some of it will be located elsewhere without a Pt neighbor (decreasing Mo-Pt, the average number of Pt scatterers around a Mo). This second assertion is supported by the fact that the coordination of the light scatterer to Mo (oxide or carbide) increases with increasing Mo content.

Table 5. EXAFS fits for the Pt L_{III} edge assuming molybdenum carbide.

Sample	Description	Scatterer	N	R (Å)	$\sigma^2 \times 10^3$ (Å ²)	Eo (eV)
CS-PtMo/C-1	CS 1 cycle	Pt-Pt	7.4	2.74	2	-1.4
		Pt-Mo	1.6	2.73	2	9.5
CS-PtMo/C-2	CS 2 cycle	Pt-Pt	7.6	2.74	2	-2.8
		Pt-Mo	1.9	2.73	2	9.3
CS-PtMo/C-3	CS 3 cycle	Pt-Pt	6.9	2.74	2	-2.1
		Pt-Mo	2.0	2.73	2	9.4
IWI1-PtMo/C-1	0.4% Mo	Pt-Pt	9.4	2.74	2	-1.2
		Pt-Mo	1.1	2.73	2	10.1
IWI1-PtMo/C-2	0.8% Mo	Pt-Pt	8.5	2.74	2	-2.7
		Pt-Mo	1.5	2.73	2	13.6
IWI1-PtMo/C-3	1.3% Mo	Pt-Pt	8.2	2.74	2	-2.2
		Pt-Mo	1.5	2.73	2	11.7

The estimated uncertainties are: N , $\pm 20\%$; R , ± 0.02 Å

Table 6. EXAFS fits for the Mo K edge assuming molybdenum carbide.

Sample	Description	Scatterer	N	R (Å)	$\sigma^2 \times 10^3$ (Å ²)	Eo (eV)
CS-PtMo/C-1	CS 1 cycle	Mo-C	5.5	2.12	0	-2.5
		Mo-Pt	5.5	2.73	3	-4.1
CS-PtMo/C-2	CS 2 cycle	Mo-C	7.5	2.12	0	-2.4
		Mo-Pt	2.5	2.73	3	-6.5
CS-PtMo/C-3	CS 3 cycle	Mo-C	8.4	2.10	0	-5.0
		Mo-Pt	2.1	2.73	3	-7.8
IWI1-PtMo/C-1	0.4% Mo	Mo-C	7.1	2.10	0	-6.0

IWI1-PtMo/C-2	0.8% Mo	Mo-Pt	3.2	2.73	3	-5.6
		Mo-C	8.6	2.10	0	-5.2
IWI1- PtMo/C-3	1.3% Mo	Mo-Pt	2.4	2.73	3	-5.3
		Mo-C	8.6	2.09	0	-5.5
		Mo-Pt	2.4	2.73	3	-5.7

The estimated uncertainties are: N , $\pm 20\%$; R , $\pm 0.02 \text{ \AA}$

Importantly, whether the Mo is fit with an oxide or carbide scatterer, the only metallic scattering is with Pt, and no Mo-Mo scattering was detected. This lack of Mo-Mo scattering indicates small amounts of Mo on the Pt nanoparticles or small nanoparticles of isolated Mo, because larger agglomerations would show Mo-Mo bonds (in the case of carbides) or the typical Mo=O double bonds found in unreduced MoO_x .

3.2.3 RhRe System

The characterization results for the RhRe/C catalysts are presented in Table 7. The CO uptake is decreased by 34% upon the addition of a small amount of Re to obtain an atomic ratio of Rh:Re= 1:0.12 (CS-RhRe/C-1). This behavior is consistent with both RhMo and PtMo system. Thus the synthesis of bimetallic catalysts by the CS procedure for all the three RhMo, PtMo and RhRe systems results in a decrease of CO uptake compared to the monometallic Rh/C or Pt/C.

Table 7. RhRe characterization results.

Catalyst ID	Details	At. Rh:Re (ICP)	Rh wt% (ICP)	Re wt% (ICP)	At. Rh:Re (EDS)	Rh sites ($\mu\text{mol g}^{-1}$) ^a
Rh/C	Parent catalyst by WI	-	4.50	0	N/A	226.7
CS-RhRe/C-1	CS - 1 cycle	1:0.12	3.37	0.73	1:0.17	148.8
CS-RhRe/C-2	CS - 1 cycle	1:0.17	3.64	1.11	-	146.5
CS-RhRe/C-3	CS - 1 cycle	1:0.73	3.50	4.64	-	149.5
CS-RhRe/C-4	CS - 1 cycle	1:1.20	3.57	7.77	-	127.7

^a assuming 0.75 ML coverage of CO at full saturation [25]

As was done for the PtMo system, EDS analysis was also performed for a RhRe/C CS catalysts with Rh:Re= 0.12 (CS-RhRe/C-1). A number averaged composition considering around 30 particles for the analysis is presented in Table 7, showing good agreement between the ICP and EDS determined compositions, indicating homogeneity in bimetallic composition for this smaller Re loadings.

3.3 Reactivity results

3.3.1 RhMo System

A suitable probe reaction for catalytic study is the selective CO hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran (HMTHP) (Scheme 1). In our previous work, we reported that depending upon the type of oxophilic promoter used, the reaction rates to selectively produce 1,6-hexanediol (1,6-HDO) are promoted from 6 fold (for Mo) to 23 fold (for Re) compared to the monometallic catalyst [25, 26]. The reactivity results for RhMo catalysts are summarized in Table 8. It should be noted that all the catalysts within a series contain similar amount of Rh, with varying Mo content to study an effect of composition on the reactivity in a consistent fashion.

The monometallic 4.5 wt% Rh/C catalyst displays a low rate for the conversion of HMTHP along with poor selectivity for the formation of 1,6-HDO. The addition of Mo as an oxophilic promoter in quantities as small as 0.05 wt% Mo to give a Rh:Mo atomic ratio of 1:0.01 (CS-RhMo/C-1) resulted in a promotion of the rates by 3 times and increased selectivity to 1,6 HDO exceeding 80%. The change in rate and selectivity indicates that the addition of Mo has fundamentally changed the nature of the active sites. Increasing the Mo content to 0.1 wt% (Rh:Mo=1:0.03 (CS-RhMo/C-2)) leads to further promotion in the rate compared to monometallic Rh/C by a factor of 12, while keeping the same high level of selectivity (80%) to 1,6-HDO, indicating that the addition of more Mo increases the number of new active sites without fundamentally altering them. This increase in rate with increasing Mo content continued until a maximum rate of around $30 \mu\text{mol g}^{-1} \text{min}^{-1}$ was achieved for the CS catalyst with Rh:Mo of 1:0.1 (CS-RhMo/C-4) was achieved. The rate remained constant with further increase in the Mo content until the Rh:Mo composition of 1:0.3 (CS-RhMo/C-7), subsequent to which the rate was observed to decrease

with increasing Mo content. For CS RhMo/C catalyst with Rh:Mo= 1:0.4 (CS-RhMo/C-8) prepared in three cycles, the rate decreased to 25 $\mu\text{mol g}^{-1} \text{min}^{-1}$. The rate using the CS catalysts prepared in 4 cycles with a ratio Rh:Mo= 1:0.45 (CS-RhMo/C-9) further decreased to around 19 $\mu\text{mol g}^{-1} \text{min}^{-1}$.

For the catalyst that was prepared in a single cycle rather than multiple cycles to achieve a higher Mo loading of 2.3 wt% (Rh:Mo= 1:0.67 (CS-RhMo/C-12)), the rate was found to be lower at 14 $\mu\text{mol g}^{-1} \text{min}^{-1}$. As mentioned previously, the EDS analysis of the individual particles indicated a number average value of 22.2% for the Mo atomic composition indicating Rh:Mo= 1:0.28, which is lower than the ICP determined overall composition. This behavior suggests that a significant portion of the Mo is on the support and was not accounted for in the EDS analysis of individual particles, and that there are a smaller number of bimetallic particles with above mentioned composition leading to lower rates.

Table 8. Reactivity summary of RhMo catalysts.

Catalyst ID	Details	At. Rh:Mo (ICP)	Conversion (%)	1,6-HDO Select (%)	Rate ($\mu\text{mol gcat}^{-1} \text{min}^{-1}$)	TOF x 10^3 (min^{-1})
Rh/C	Parent catalyst by WI	-	1.5	15.6	0.9	4.0
CS-RhMo/C-1	CS - 1 cycle	1:0.01	4.3	84.0	2.7	13.9
CS-RhMo/C-2	CS - 1 cycle	1:0.03	12.6	80.1	11.9	64.6
CS-RhMo/C-3	CS - 1 cycle	1:0.06	22.2	77.9	19.3	99.6
CS-RhMo/C-4	CS - 1 cycle	1:0.11	31.9	79.6	30.3	162.3
CS-RhMo/C-5	CS - 1 cycle	1:0.16	35.2	77.4	31.5	190.8
CS-RhMo/C-6	CS - 2 cycles	1:0.15	39.8	80.4	33.4	191.1
CS-RhMo/C-7	CS - 3 cycles	1:0.28	35.8	81.6	31.3	231.6
CS-RhMo/C-8	CS - 3 cycles	1:0.40	29.7	82.4	25.1	288.3
CS-RhMo/C-9	CS - 4 cycles	1:0.45	21.1	83.0	18.6	329.4
CS-RhMo/C-12	CS - 1 cycle	1:0.67	15.2	84.0	14.5	175.2

To gain insight into the nature of active sites, the turnover frequencies (TOFs) were also calculated (as determined by CO chemisorption) and plotted against the Mo content in Fig. 10(a). For the CS catalysts, there was a continuous increase in the TOF. The sites measured by CO chemisorption measure the exposed Rh atoms, not all of which constitute the active sites, as we know from the control experiment using a monometallic Rh/C catalyst. Upon addition of higher amounts of Mo, the rates per gram increase while the CO uptake decreases. Once the maximum in the rate per gram is attained, the rate per gram begins to decrease, but so does the CO uptake which leads to a continuous increase in the TOF. Thus, we can infer that a Mo content of around 10 wt% (where the rate per gram is maximized) is sufficient to obtain the best performance from the bimetallic catalyst. Any additional Mo does not contribute to the creation of more active sites and does not enhance the rates per gram. The upward trend in TOF is due to surface coverage of Rh by Mo and a lower number of exposed Rh atoms.

Fig. 10. Turnover frequencies (min^{-1}) versus oxophilic promoter content in various (a) RhMo, (b) PtMo and (c) RhRe bimetallic catalysts, inset presents a plot of rate per gram of catalyst versus promoter content.

3.3.2 PtMo system

The catalytic activities of the synthesized PtMo/C catalysts were also evaluated for the HMTHP hydrogenolysis reaction. The reactivity results are summarized in Table 9 and in Fig. 10(b). Similar to the

monometallic Rh/C catalyst, the monometallic Pt/C catalyst displayed minimal activity for the reaction, along with a poor selectivity to 1,6 HDO. For the CS catalysts, on addition of Mo to obtain a Pt:Mo atomic ratio of 1:0.18 (CS-PtMo/C-1), there was small promotion in the reaction rate per gram catalyst (Table 9). Further increasing the Mo content in two cycles to obtain Pt:Mo= 1:0.3 (CS-PtMo/C-2), leads to further promotion of the rate per gram catalyst by 5 times and a 1,6-HDO selectivity of 75%. Because the decrease in the CO uptake with further increase in the Mo content was not significant, the increase in TOF for 1:0.3 catalyst was also 5 fold. For the CS catalyst prepared in three cycles to produce a bimetallic composition of Pt:Mo= 1:0.48 (CS-PtMo/C-3), the reaction rate was observed to be 7 times higher than Pt:Mo= 1:0.18 CS catalyst (CS-PtMo/C-1). Again, because a similar CO uptake was achieved, the TOF was also 7 times higher.

For comparison, a CS catalyst with higher Mo content (Pt:Mo= 1:0.6) (CS-PtMo/C-4), that was prepared in a single step, showed a lower reactivity (Table 9, Fig. 10(b)). This lower rate is expected, because the actual bimetallic composition in the individual particles is Pt:Mo= 1:0.24 (Table 2), which is lower than the ICP determined overall value. In fact, the rate per gram is similar to the CS-PtMo/C-2 catalyst which has a similar Pt:Mo ratio by STEM/EDS. Thus, to synthesize a catalyst with higher Mo content, the CS should be performed in multiple cycles for Mo containing catalysts.

Table 9. Reactivity summary of PtMo catalysts.

Catalyst ID	Details	At. Pt:Mo (ICP)	Conversion (%)	1,6-HDO Select (%)	Rate ($\mu\text{mol gcat}^{-1} \text{min}^{-1}$)	TOF x 10^3 (min^{-1})
Pt/C	Parent catalyst by WI	-	1.1	14.8	0.5	4.1
CS-PtMo/C-1	CS - 1 cycle	1:0.18	1.3	44.0	1.1	16.7
CS-PtMo/C-2	CS - 2 cycles	1:0.31	6.7	74.6	5.6	78.2
CS-PtMo/C-3	CS - 3 cycles	1:0.48	8.3	75.6	7.1	116.6

CS-PtMo/C-4	CS - 1 cycle	1:0.60	5.8	85.5	5.5	93.3
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3.3.3 RhRe system

The performance of the RhRe catalysts in the selective CO hydrogenolysis of the HMTHP is presented in Table 10 and in Fig. 10(c). The addition of a small amount of Re to obtain catalysts with composition Rh:Re= 1:0.12 (CS-RhRe/C-1), resulted only in a small promotion of the reaction rate per gram of catalyst, similar to the behavior observed on PtMo/C, possibly indicating that clusters of the oxophilic metal were not sufficiently large to generate the active site at such low loadings. Further increasing the Re content to obtain composition 1:0.17 resulted in an increase in the reaction rate by 5 fold. Due to a similar CO uptake, the increase in the TOF was also 5 fold (Fig. 10(c)). For the CS catalysts with the composition of 1:0.73 (CS-RhRe/C-3), there was a significant increase in the rate (16 fold) and in the corresponding TOF, since the CO uptake was similar. This rate is the highest reaction rate achieved of the three catalyst systems: RhMo, PtMo and RhRe considered in the present work. Moreover, the selectivity to 1,6-HDO was around 85-90%, which is also the best selectivity of the three bimetallic systems. Upon further increasing the Re content to obtain a composition of Rh:Re= 1:1.2 (CS-RhRe/C-4), the rate decreased.

Table 10. Reactivity summary of RhRe catalysts.

Catalyst ID	Details	At. Rh:Re (ICP)	Conversion (%)	1,6-HDO Select (%)	Rate ($\mu\text{mol gcat}^{-1} \text{min}^{-1}$)	TOF x 10^3 (min^{-1})
Rh/C	Parent catalyst by WI	-	1.5	15.6	0.9	4.0
CS-RhRe/C-1	CS - 1 cycle	1:0.12	1.3	35.6	3.9	26.3
CS-RhRe/C-2	CS - 1 cycle	1:0.17	6.4	76.5	18.8	128.4
CS-RhRe/C-3	CS - 1 cycle	1:0.73	14.1	85.6	61.4	411.0
CS-RhRe/C-4	CS - 1 cycle	1:1.20	7.7	91.5	37.1	290.2

4. Discussion

Based on the results from the characterization and reactivity measurements for the CS catalysts, we propose the following hypothesis of the nature of active sites involved in the selective hydrogenolysis reaction. The active sites on RhMo and PtMo catalysts for the selective hydrogenolysis of cyclic ethers consist of a small ensemble of Rh or Pt atoms adjacent to a highly reduced Mo moiety that is coordinated to the precious metal nanoparticle. While the highly reducible metal (Rh or Pt) provides the hydrogenation sites, an adjacent oxophilic promoter provides an acid functionality in this bifunctional catalyst [25, 26].

In the case of PtMo the Mo is also coordinated to a light scatterer (i.e., C or O). The active site does not necessarily require a large ensemble of Rh or Pt surface atoms as indicated by the FTIR spectrum of CO adsorbed on an active RhMo catalyst, which shows the predominance of CO species on atop sites and the absence of bridge-bonded CO. It is also sufficient to have small ensembles of Mo atoms on the surface to produce an active site according to the lack of Mo-Mo coordination in the promoted PtMo catalysts.

When Mo loading is low, we see from the EXAFS results (Table 4 and Table 6) that the coordination of the Mo moieties in the PtMo catalysts has a predominance of Mo-Pt neighbors. Accordingly, we suggest that the Mo species are present preferentially within the Pt nanoparticles at low Mo loadings, leading to the presence of Mo-Pt bonds. A fraction could also be present on the nanoparticle surface and on the support, as indicated by the Mo coordination to the light scatterer. It should be noted that the XAS results were obtained under a reducing atmosphere, which thermodynamically drives the oxophilic promoter to stay subsurface [26, 34]. Even if structural rearrangement takes place under the reaction conditions, the small extent to which the catalytic activity is promoted for catalysts with a low Mo content suggests that a small number of surface active sites have been formed. These catalysts also

display higher CO uptake due to a large number of exposed Rh atoms on the surface as well as a large number of bridged-bonded CO species, suggesting large Rh ensembles.

When the loading of the Mo is increased, higher concentrations of Mo species located at the surface of the Pt nanoparticles are achieved, leading to an increase in the Mo coordination by light scatterers. This change in coordination environment is accompanied by an increase in the rate per gram of Pt-Mo catalyst, as well as an increase in rate per Pt site, as titrated by CO chemisorption. The presence of surface Mo also decreases the size of surface Rh ensembles, resulting in a decrease in the bridged-bonded CO as observed by FTIR analysis. The increase in rate can thus be correlated with the increase in surface concentration of these Mo, an assertion supported by previous theoretical work [35]. As long as the surface concentration of these Mo species remains low (as it does for the PtMo system in this study), the rate per surface area and the rate per Pt surface atom continue to increase as Mo loading of the catalyst increases.

When the Mo content is further increased for the RhMo system, the number of active sites is eventually decreased and the rate per gram catalyst declines. Thus, the rate per gram of the RhMo catalyst passes through a maximum with respect to the Mo loading, indicating that a Rh-Mo nanoparticle can become highly covered by Mo-species, leading to a decrease in the number of active sites. (We note that the rate per gram of the Rh-Mo catalyst is proportional to the rate per metallic surface area of the nanoparticles, because the Rh-Mo catalysts prepared by the CS method always start with the same Rh/C parent catalyst.) In contrast, when the rate is normalized by the number of surface Rh atoms, as measured by CO chemisorption, then the turnover frequency for hydrogenolysis continues to increase with Mo loading. This behavior indicates that along with a decrease in the number of active sites due to high coverage by Mo, the higher fraction of the Rh surface atoms are now adjacent to a Mo moiety, hence increasing the TOF based on the CO uptake. The high coverage of Mo resulted in a disappearance of the bridged-bonded CO as observed by the FTIR analysis, indicating that very small Rh ensembles are sufficient to constitute an active site. This result suggests the possibility that developing a CS technique

to instead add small amounts of the expensive highly reducible metal (Rh) to an oxophilic (Mo) nanoparticle may lead to the most efficient utilization of the more expensive component of the catalyst.

In summary, a small ensemble of highly reducible metal atoms adjacent to a small ensemble of highly reduced moieties of an oxophilic promoter provides the best scenario for the active site. Larger ensembles of reducible metal are not necessary, and indeed, smaller ensembles allow a higher fraction of the hydrogenating element to be adjacent to the oxophilic acid functionality. Similarly, large clusters of oxophilic promoters on the surface of the nanoparticle are not active by themselves, but rather they cause a decrease in the number of active sites by covering the hydrogenating metal atoms.

5. Conclusions

We show that the strength of interaction between the reducible metal and the organometallic precursor of the oxophilic promoter is important to synthesize bimetallic catalysts using a controlled synthesis (CS) approach. In addition, there is a limitation to the amount of oxophilic promoter than can be added in the bimetallic catalyst by this approach. In particular, for RhMo system, the adsorption of organometallic $(C_7H_8)Mo(CO)_3$ precursor occurs rapidly and selectively onto Rh nanoparticles, indicating strong affinity of the Mo cluster with Rh. However, the uptake becomes slower with successive cycles, because of the availability of a smaller number of surface Rh atoms and a weaker affinity of the precursor with surface Mo. The adsorption of organometallic $(C_5H_5)Re(CO)_3$ on Rh was weaker compared to the $(C_7H_8)Mo(CO)_3$ precursor.

We suggest that the active sites in the bifunctional RhMo and PtMo systems consist of small ensemble of Rh or Pt atoms adjacent to a highly reduced Mo moiety. When the Mo loading is low, the coordination of the Mo moieties in the PtMo catalysts has a predominance of Mo-Pt neighbors, indicating that a fraction of Mo may be located subsurface. Thus, the extent of promotion of catalytic activity at these low Mo levels is small. When the loading of the Mo is increased, a higher fraction of the Mo species is located at the surface of the Rh or Pt nanoparticles, which is correlated to more extensive promotion in

the reactivity by creation of new bifunctional active sites. The rate per gram catalyst and the rate per Rh or Pt surface atom continue to increase as Mo loading of the catalyst increases, as long as the surface concentration of these Mo species remains low. At higher Mo content, the Rh-Mo or Pt-Mo nanoparticles can become highly covered by Mo-species, leading to a decrease in the number of active sites and a decrease in the rate per surface area. However, the turnover frequency, based on the decreasing CO uptake, remains high at these high Mo levels. These results suggest that the most active catalysts consist of nanoparticles with bifunctional active sites composed of the maximal number of small ensembles of Rh or Pt (for hydrogenation) and small ensembles of Mo or Re (for the generation of acidity) in close proximity.

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