Synthesis of Supported RhMo and PtMo Bimetallic Catalysts by Controlled Surface Reactions

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We previously described a synthesis method to prepare bimetallic catalysts with narrow nanoparticle size and composition distributions by means of controlled surface reactions (CSR) between a reduced supported metal nanoparticle and an organometallic precursor of an oxophilic promoter metal. Herein, we report a comparison of such catalysts with those prepared by traditional incipient wetness impregnation. STEM/EDS analysis indicates that catalysts prepared by CSR exhibit more effective interaction of metals, thereby minimizing the undesirable formation of component-rich nanoparticles and/or monometallic domains. Reaction kinetics studies using these bimetallic catalysts reveal that optimal conversion rates in a selective CO hydrogenolysis reaction (i.e., hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran to 1,6-hexanediol) could be achieved using a lower amount of the oxophilic promoter metal for the catalysts prepared by the CSR approach, as compared to their impregnated counterparts.

Introduction

For the past several decades, supported bimetallic catalysts have been studied extensively in heterogeneous catalysis research because they offer significantly improved catalytic activity, selectivity and stability in comparison with their monometallic counterparts.^[1] Supported bimetallic catalysts have been employed in several well-studied reaction systems, such as water-gas shift,^[2-4] higher-alcohol synthesis,^[5-10] Fischer-Tropsch synthesis,^[11,12] and direct synthesis of hydrogen peroxide.^[13,14] In addition, bimetallic catalysts have been shown to exhibit enhanced performance for reactions involved in the conversion of biomass into chemicals and fuels.^[15] for example. in selective CO hydrogenolysis.[16-19] Traditional methods of supported bimetallic catalysts preparation, such as incipient wetness impregnation (IWI), can produce nanoparticles with inherently non-uniform particle sizes and compositions. This complexity makes it difficult to establish structure-reactivity correlations, because most characterization techniques provide information that is representative of the overall sample. In this context, it is important to develop new synthesis strategies that produce supported bimetallic nanoparticles with well-defined size and composition. A variety of synthesis approaches have been suggested to accomplish this goal.^[20-25] We recently developed a synthesis protocol that utilizes controlled surface reactions (CSR) between a reduced supported metal (denoted as the parent catalyst) and a specific organometallic precursor

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500767. of an oxophilic promoter metal in an organic solution. The details of this facile approach to catalyst synthesis employing CSR can be found in our previous work.^[17]

Incipient wetness impregnation (IWI) is a standard approach to synthesize supported metal catalysts; therefore, in this work, we have synthesized RhMo/C and PtMo/C catalysts using IWI methods and we have compared these materials with those that were prepared by the CSR technique. We have identified and discussed the differences between these materials by means of structural characterization and catalytic reactivity measurement studies.

Results and Discussion

The as-synthesized CSR and IWI catalysts were characterized by CO chemisorption, ICP and STEM/EDS analysis. The structural characterization results for different RhMo/C and PtMo/C catalysts prepared are summarized for comparison in Tables 1 and 2. In all cases, the amount of the highly reducible component (Rh, Pt) was kept constant in the parent catalyst, and the amount of the oxophilic promoter (Mo) was varied during the preparation of catalysts to obtain different metal ratios. All presented ratios are atomic (or molar) ratios, and the theoretical ratio is based on the initial amount of precursor added during the synthesis. Two variations of IWI method (IWI1, co-impregnation and IWI2, sequential impregnation) were studied, the details of which can be found in the experimental section.

As can be seen in Table 1, for both CSR and IWI catalysts, the number of exposed surface Rh metal sites, as characterized by CO chemisorption, was found to decrease after Mo addition. This decrease is caused as the exposed noble metal becomes progressively covered by an increasing content of the oxophilic element. This result suggests that it is possible to

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Catalyst ID	At. Mo/Rh Theo.	Rh sites [µmol g ⁻¹]	Rh [wt%]	ICP ^[a] Mo [wt %]	At. Mo/Rh	EDS ^[b] At. Mo/Rh
Rh/C	0	226.7	4.50	0	_	N/A
CSR-RhMo/C-4 ^[17]	0.1	186.9	4.10	0.42	0.11	0.10
CSR-RhMo/C-6 ^[17]	0.15	174.7	4.35	0.61	0.15	0.17
CSR-RhMo/C-7 ^[17]	0.3	134.9	4.50	1.17	0.28	0.25
CSR-RhMo/C-9 ^[17]	0.6	56.4	4.32	1.82	0.45	0.24
IWI1-RhMo/C-1	0.1	203.7	3.91	0.36	0.1	0.16
IWI1-RhMo/C-2	0.36	145.3	3.33	1.19	0.38	0.22
IWI1-RhMo/C-3	1	61.2	3.10	3.36	1.16	0.35
IWI2-RhMo/C-1	0.1	160	-	-	-	-
IWI2-RhMo/C-2	0.36	119.6	3.53	1.17	0.35	0.23
IWI2-RhMo/C-3	1	50.5	3.37	3.56	1.13	0.57

Table 2. Structural characterization results for PtMo/C catalysts prepared by controlled surface reactions (CSR) and incipient wetness impregnation (IWI).										
Catalyst ID	At. Mo/Pt Theo.	Pt sites [μmol g ⁻¹]	Pt wt%	ICP ^[a] Mo wt %	6 At. Mo/Pt	EDS ^[b] At. Mo/Pt				
Pt/C CSR-PtMo/C-1b CSR-PtMo/C-2b CSR-PtMo/C-3b CSR-PtMo/C-4b CSR-PtMo/C-5b IWI1-PtMo/C-1 IWI1-PtMo/C-2 IWI1-PtMo/C-3 IWI2-PtMo/C-2 IWI2-PtMo/C-3	0 0.15 0.3 0.45 0.6 0.75 0.3 0.45 0.6 0.3 0.45 0.6	200.0 112.4 101.6 69.9 77.3 84.3 123.5 86.7 - 103.3 101.3 92.0	4.93 4.40 4.22 4.37 4.61 4.50 4.51 - 3.66 4.40 4.48 4.15	0 0.37 0.69 1.02 1.23 1.35 0.65 - 1.23 0.71 1.03 1.42	- 0.17 0.33 0.47 0.54 0.61 0.3 - 0.68 0.34 0.54 0.70	N/A 0.11 0.21 0.34 0.30 0.32 0.18 0.21 0.23 0.21 0.28 0.33				
[a] ICP = Inductively coupled plasma-atomic emission spectroscopy (ICP-AES). [b] EDS = energy dispersive X-ray spectroscopy.										

obtain alloys with both synthesis techniques. We note here that the usage of term "alloy" is meant to denote the intimate contact between the two metals, and it is not suggested to mean uniform ordering of constituent metals as defined in metallurgy.

STEM/EDS analyses were performed to compare the physical properties of catalysts prepared by CSR and IWI methods. Single spot EDS analyses of around 30 to 50 particles for each catalyst were considered to obtain a number averaged value that can be compared with the corresponding ICP values. Figure 1 shows STEM images obtained for one of the CSR catalysts, as an example of the nanoparticles that were found and analyzed by EDS. During our initial study,^[17] we consistently observed that the EDS values for the nanoparticles indicated a lower content of the oxophilic metal (Mo or Re) as compared to the overall ICP values. STEM imaging revealed single atoms of the oxophilic metal over the C support, and also over the TEM grid (Figure 2). The solubility and volatility of oxophilic metal oxides is well known,^[26] and if not carefully handled may lead to misleading results, as we found earlier in this study.

The final passivation step during the catalyst synthesis leads to the oxidation of the oxophilic metal. Subsequently, the oxophilic metal oxide is leached into the ethanol solution used to disperse the solid catalysts onto the TEM grids. To remedy this problem, we adopted the procedure illustrated schematically in Figure S1, Supporting information. The bimetallic catalyst was reduced in a Schlenk tube, and after sealing, it was transferred to the glove box maintained under N₂ atmosphere. Inside the glove box, the solid was dispersed in anhydrous ethanol and deposited over the TEM grid after evaporation of the solvent. Once this precaution was taken to prepare the samples for STEM/EDS analysis, such dispersed single atoms were not observed for either Mo or Re containing catalysts, and the EDS values displayed a better match with ICP values.

Results from STEM/EDS analyses of the CSR-RhMo/ C catalysts showed good agreement between the atomic compositions from ICP and EDS measurements for Mo/Rh atomic ratio up to 0.3. This agreement between ICP (bulk analysis) and EDS (by individually considering around 30-50 nanoparticles and presenting their number averaged composition values) provides evidence that the CSR method successfully produces bimetallic catalysts with excellent uniformity in the nanoparticle composition. The ICP and EDS values, however, showed differences for higher Mo loadings (Mo/Rh = 0.6), which can be attributed to the saturation of the Rh nanoparticles by Mo.^[17] By comparing the ICP and EDS values for IWI catalysts in Table 1, it can be seen that EDS values in individual particles for the IWI catalysts appear to be skewed towards higher Rh content. The overall ICP values agree well with the theoretical ratio, but the EDS values show lower Mo content, indicating nonuniformity in composition of IWI nanoparticles on

catalyst surface, with the presence of surface Mo domains that are not accounted for in the analysis of individual particles by STEM/EDS. No significant differences between the impregnation variations IWI1 and IWI2 catalysts could be ascertained.

The differences between CSR and IWI RhMo/C catalysts were further highlighted when composition distribution plots were prepared.^[17] Although the CSR catalysts displayed narrow dis-



Figure 1. STEM images of CSR-PtMo/C-2b catalyst.

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Figure 2. STEM images of a RhRe/C sample showing evidence of leaching of the oxophilic component on a) the support (carbon) and b) over the TEM grid.

tributions with composition maxima centered at the ICP determined value, the distributions for IWI catalysts were found to be broader with maxima displaced from the ICP determined overall composition value towards lower Mo content.

A second bimetallic system, PtMo/C, was also studied for the comparison of the CSR and IWI techniques. A 5 wt% Pt/C was prepared and used for CSR, IWI1, and IWI2 syntheses. In our previous work, we observed that a lower molar loading of Pt compared to Rh on the carbon support possibly led to a higher availability of unoccupied defects sites on the carbon support available for binding to the Mo precursor, resulting in a mismatch between ICP and EDS values for CSR-PtMo/C catalysts even for low Mo loadings.^[17] Here in Table 2 we demonstrate that by using higher loading of Pt, most of the defect sites on the carbon support were occupied by Pt atoms, and the organometallic Mo precursor then selectively binds to reduced Pt atoms on the surface, resulting in an efficient alloying and a better match between ICP and EDS values, especially for the lower Mo loadings.

A comparison of CO chemisorption values for CSR-PtMo/C catalysts shows a decrease in CO uptake, owing to progressive coverage of the exposed Pt by increasing the content of Mo up to a Mo/Pt ratio of 0.3, beyond which the uptake remains unchanged. This behavior is confirmed by comparing the ICP and EDS values for CSR-PtMo/C catalysts in Table 2, where the ICP values remain consistent with the initial theoretical amount added for increasing Mo content, whereas the EDS determined values are nearly constant beyond Mo/Pt=0.3. IWI1-PtMo/C catalysts were particularly poor in terms of their much lower Mo content in EDS analyzed nanoparticles. These results indicate that Mo has a lower affinity for Pt as compared to Rh, such that with additional cycles to increase the Mo content, the deposition of Mo selectively onto the Pt metal nanoparticles becomes progressively less efficient. Additionally, the maximum Mo content for the IWI1 catalysts was lower than in the CSR catalysts. IWI2 catalysts, on the other hand, appeared to be more similar to their CSR counterparts based on the comparison of ICP and the number averaged EDS values.

Composition distribution plots were also prepared using the STEM/EDS data for CSR and IWI PtMo/C catalysts (Figure 3). Consistent with the observations from Table 2, the maxima of the EDS determined composition values were skewed towards

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Figure 3. EDS-determined composition distributions of PtMo/C catalysts: a) comparison of CSR (CSR-PtMo/C-2b), IWI1 (IWI1-PtMo/C-1), and IWI2 (IWI2-PtMo/C-1) catalysts for a bimetallic composition of Mo/Pt=0.3, b) comparison of CSR (CSR-PtMo/C-3b), IWI1 (IWI1-PtMo/C-2), and IWI2 (IWI2-PtMo/C-2) catalysts for a bimetallic composition of Mo/Pt=0.45, and c) comparison of CSR (CSR-PtMo/C-4b), IWI1 (IWI1-PtMo/C-3), and IWI2 (IWI2-PtMo/C-3) catalysts for a bimetallic composition of Mo/Pt=0.45, and c) comparison of CSR (CSR-PtMo/C-4b), IWI1 (IWI1-PtMo/C-3), and IWI2 (IWI2-PtMo/C-3) catalysts for a bimetallic composition of Mo/Pt=0.6. Average EDS values \pm standard deviations are shown in the legends for easier comparison. Vertical lines in the plots indicate the ICP-AES values (or theoretical values for the two catalysts when no ICP values were available, since ICP and theoretical values based on the amount of Mo/Pt ratios in the legends are the theoretical values based on the amount of Mo/Pt ratios in the organic solution.

lower Mo content as compared to the overall ICP values for all the three synthesis techniques. Unlike in the RhMo/C system, no clear distinction for the CSR-PtMo/C catalysts could be ascertained just based on these composition distribution plots. It



can be observed in Figure 3 that standard deviations from the average value are similar for the different techniques and Mo loadings. Moreover, it is clear that effective interaction between Pt and Mo is only achieved at Mo/Pt ratios lower than 0.3. The advantage of selective deposition of organometallic precursor of oxophilic metal onto the pre-reduced noble metal in the parent catalyst that the CSR method offers is reduced when there is weak interaction between the precursor and reduced metal surface. Although the differences in composition distributions for CSR and IWI catalysts were significant for RhMo/C system,^[17] which is characterized by a strong interaction between the two metals, they appear to be less significant for the PtMo/C system with a weaker interactions.

To further study the differences between CSR and IWI catalysts, the catalytic activities of the different catalysts for the RhMo/C and PtMo/C systems were evaluated in the selective CO hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran (HMTHP) to 1,6-hexanediol (Scheme 1). In our previous work, it was concluded that the most active catalysts for this reaction consist of nanoparticles with bi-functional active sites composed of small ensembles of the highly reducible metal (Rh or Pt for hydrogenation) and small ensembles of the oxophilic element (Mo or Re for the generation of acidity) in close proximity.^[17]



Scheme 1. Reaction Scheme of 2-(hydroxymethyl)tetrahydropyran (HMTHP) hydrogenolysis.

Figure 4a plots the specific rate per gram of catalyst for the RhMo/C system with respect to the Mo content (ICP value). The plot of specific rate versus Mo level shows a bell-shaped curve. It can be seen that the addition of around 10 at% Mo (ICP value) using the CSR approach was sufficient to achieve the maximum promotion, beyond which there was an accumulation of Mo at the surface that did not contribute to the formation of active site but rather reduced the number of existing active sites by covering the Rh surface. An important observation is that the specific rate maxima for IWI1 and IWI2 are displaced to a higher Mo loading (~25 at % Mo, ICP value). This displacement is a strong indication of efficient alloying and uniformity in the CSR catalysts, where targeted deposition of oxophilic component resulted in a smaller amount of Mo being sufficient to achieve similar conversion rates. Compositional non-uniformity for the IWI catalysts required a higher loading of oxophilic promoter to create the same number of bi-functional active sites, because inherently nanoparticles rich in either component or monometallic particles were formed that do not contribute to improving the catalytic reactivity. This result demonstrates the superiority of CSR catalysts as compared to IWI catalysts. The CSR catalysts are more suitable as model bimetallic materials for the study of the effect of component ratio and in the elucidation of nature of active sites in conjunction with theoretical studies. Additionally, CSR catalysts are beneficial from an economical point of view, where targeted deposition results in saving of the expensive oxophilic promoters such as rhenium.

Specific reactivity plots for PtMo/C catalysts are presented in Figure 4b. These plots of specific rate versus Mo level also demonstrate a bell-shape curve for the CSR catalysts, indicating the creation of bi-functional active sites as Mo is progressively deposited, followed by the blocking of the Pt surface at higher Mo levels. Thus, it can be concluded that even with a lower affinity of Mo for Pt, the deposition of Mo onto the Pt nanoparticle surface can be achieved to create a maximum in the number of active sites for this system. Although the CSR catalysts show a bell-shaped curve in the plot of specific rate versus composition, the specific rate curves for the IWI catalysts are rather broad, and a clear maximum in the rate is not observed. This behavior suggests inefficient alloying in the IWI catalysts, resulting in a wide range of composition distribution such that the promotional effect of increasing Mo content is

> less responsive to composition change. Therefore, even for a system with a weaker affinity between the bimetallic components, CSR catalysts demonstrate more efficient alloying and result in a more uniform nanoparticle composition as compared to IWI catalysts.

> The differences between catalyst synthesis methods are further compared based on turnover frequencies (rates normalized by exposed noble metal) (Figure 5a and b). For the RhMo system, a continuous upward trend in TOF for the catalysts prepared by CSR can be attributed to the fact that the specific rate increases with Mo loading, while the number of exposed Rh surface atoms decreases. This behavior is

an indication of effective alloying by means of selective deposition of Mo onto the metal nanoparticles. However, different trends were obtained for those catalysts prepared by incipient wetness impregnation (IWI1 and IWI2). In this case, the initial increase in specific rate is identical to the CSR system, where the rate increases and the number of exposed Rh surface atoms decreases, resulting in an increase in TOF. However, on further increasing the Mo content, the TOF decreased. This behavior is a further evidence of broader composition distributions for the IWI catalysts, suggesting the presence of Rh rich particles along with surface Mo rich domains, the former contributing to a smaller reduction in the exposed Rh but not contributing to an increase in activity. A bell shaped curve can be also observed for the CSR-PtMo/C catalysts, as a result of the broader composition distribution in comparison with CSR-RhMo/C catalysts.

Selected spent catalysts were also characterized after reaction. Samples after reaction were filtered, washed with milli-Q water and acetone, and dried before CO chemisorption analy-





Figure 4. Rate per gram of catalyst versus atomic % Mo for a) RhMo catalysts, and b) PtMo catalysts prepared by CSR, IWI1, and IWI2.

ses. Two of the RhMo samples, and two of the PtMo samples were analyzed after reaction: CSR-RhMo/C-4 (116.5 μ mol Rh g⁻¹), CSR-RhMo/C-7 (137.5 μ mol Rh g⁻¹), CSR-PtMo/C-1b (67.6 μ mol Rh g⁻¹), and CSR-PtMo/C-3b (69.6 μ mol Rh g⁻¹). Catalysts with higher Mo loadings showed similar numbers of Rh or Pt sites after reaction as compared to those before reaction (Tables 1 and 2). A small reduction was observed in the number of exposed sites on the catalysts with low Mo loading, suggesting that the addition of Mo increases the stability of the catalysts.

Conclusions

We have developed a catalyst synthesis method using controlled surface reactions (CSR) to overcome the non-uniformity of the catalysts prepared by traditional techniques, such as incipient wetness impregnation (IWI). A combined analysis using CO chemisorption, ICP, STEM/EDS, and reactivity measurements shows that the CSR method is superior in achieving compositional uniformity in supported bimetallic nanoparticles in RhMo/C and PtMo/C systems. The CSR technique is effective to produce model materials for a better understanding of the nature of the active sites by employing bulk measurement spectroscopy techniques and for comparison with theoretical studies targeted for discovery, development and understand-



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Figure 5. Turnover frequencies versus atomic% Mo for a) RhMo catalysts, and b) PtMo catalysts prepared by CSR, IWI1, and IWI2.

ing of supported bimetallic catalysts. The CSR procedure is also well suited for extension to ternary metal systems that can potentially enable alloying of less compatible components for catalytic property enhancement.

Experimental Section

CSR synthesis

A detailed description of the synthesis protocol can be found elsewhere.^[17] In brief, monometallic parent catalysts (Rh/C, Pt/C) are first prepared by impregnation techniques using metal salts (RhCl₃, H₂PtCl₆·6 H₂O, respectively) and a carbon support (Vulcan XC-70). The reduced parents catalysts, without contacting with air were suspended in *n*-pentane solution of an organometallic precursor ((C₇H₈)Mo(CO)₃) of the oxophilic metal. From the solution, the precursor is selectively adsorbed onto the reduced metal surface, which is subjected to a reduction step to achieve alloy formation. For obtaining higher loadings of the second metal, a strategy of multiple cycles was necessary.

Impregnation synthesis

Two different variations of this technique were studied: IWI1 catalysts were prepared by co-impregnation with the metal salt solutions (first RhCl₃ or H₂PtCl₆·6H₂O and then (NH₄)₆Mo₇O₂₄) with intermediate drying at 383 K, and a final single reduction in H₂ at 773 K,



followed by a passivation step in 1% O₂/He. IWI2 catalysts were prepared in a similar way, but with an intermediate reduction step at 773 K after drying at 383 K (sequential impregnation), resulting in a similar parent catalyst employed in the CSR method. The synthesized catalysts were designated as: Synthesis method-Metal1-Metal2/Support-Catalyst ID.

Catalyst characterization

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES): Metal contents were analyzed by ICP-AES (PerkinElmer Plasma 400 ICP Emission Spectrometer) of solutions resulting from the digestion of the catalysts in aqua regia. 20 mg of catalyst sample was weighed into a round-bottom flask followed by 10 mL of fresh aqua regia. The mixture was magnetically stirred in a silicone oil bath at 423 K under reflux for 12 h for extraction of the metals. The flask was allowed to cool after digestion and the solution vacuum filtered into a tared flask through a 0.2 micron filter with several washes of milli-Q water. The solution was typically further diluted using milli-Q water to a total weight of 50 g (low metal content samples were not diluted). Fine granules of carbon were typically still present in solution after filtration. Samples from this solution were centrifuged in 10 mL plastic centrifuge tubes at 5000 RPM for at least 5 min, decanted into fresh centrifuge tubes and centrifuged again at 5000 RPM, and the clear supernatant finally decanted into a glass vial for direct ICP-AES analysis.

CO chemisorption: These analyses were performed by using a Micromeritics ASAP2020C. A 0.75 ML coverage of CO was assumed at full saturation, and this stoichiometry was assumed constant after addition of the promoter for the sake of simplicity.

Scanning Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy (STEM/EDS): These analyses were performed by using a FEI Titan STEM with Cs probe aberration corrector operated at 200 kV. Details of the preparation of the TEM grids can be seen in the text. After deposition of the sample, carboncoated copper grids were plasma cleaned for 20 min before loading into the microscope. STEM images showing evidence of leaching of the oxophilic component were taken using a probe aberration corrected 200 kV JEOL JEM-ARM200CF microscope.

Reactivity measurement

Reactivity studies were performed in a 50 mL batch reactor (Hastelloy C-276, Model 4792, Parr instrument). The catalyst was reduced in situ at 473 K with H_2 , and then cooled to room temperature. A HPLC pump was then used to inject a 5 wt% HMTHP solution (25 mL) in milli-Q water. The reaction was performed at 393 K under stirring. The reactions were performed for a specific time to achieve similar conversion levels. The post-reaction mixture was analyzed by HPLC (Waters 2695) equipped with a differential refractometer (Waters 410), a photodiode array detector (Waters 996) and an Aminex HPX-87P column (Biorad) maintained at 358 K.

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