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Selective Adsorption of Manganese onto Rhodium for Optimized Mn/Rh/SiO₂ Alcohol Synthesis Catalysts

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Using supported rhodium-based catalysts to produce alcohols from syngas provides an alternative route to conventional fermentation methods. If left unpromoted, Rh catalysts have a strong selectivity towards methane. However, promotion with early transition metal elements has been shown to be effective to increase alcohol selectivity. Therefore, a key design objective is to increase the promoter–metal interaction to maximize their effectiveness. This can be achieved by the use of the strong electrostatic adsorption (SEA) method, which utilizes pH control to steer the promoter precursor (in this case MnO_4^-) onto Rh oxide supported on SiO₂. Mn-promoted catalysts were synthesized by both SEA and traditional incipient wetness impregnation (IWI) and subsequently characterized by

STEM and extended X-ray absorption fine structure methods. Using STEM–electron energy loss spectroscopy mapping, catalysts prepared by SEA were shown to have a higher degree of interaction between the promoter and the active metal. The reduction behavior of the catalysts obtained by X-ray absorption near-edge spectroscopy and temperature-programmed reduction demonstrated a minimal change in Rh if promoted by SEA. However, catalytic results for CO hydrogenation revealed that a significant improvement of ethanol selectivity is achieved if the promoter was prepared by SEA in comparison with the promoter prepared by IWI. These results suggest that intimate interaction between the promoter and the metal is a critical factor for improving selectivity to higher alcohols.

Introduction

Ethanol is one potential alternative synthetic fuel for use in automobiles, and the use of ethanol as a gasoline additive is already in practice both in the U.S. and internationally. Renewable ethanol can also serve as a feedstock for the synthesis of variety of industrial chemicals and polymers.^[11] However, traditional fermentation routes to alcohols are often slow and inefficient. In addition, using crops for fuel-grade alcohol production is controversial because there are doubts about its overall energy efficiency and its effect on food prices.^[2]

Several previous studies have revealed that ethanol can be produced from syngas hydrogenation over various kinds of supported metal catalysts, such as Co,^[3,4] Cu,^[5] and Pd.^[6] How-

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ever, among late d-band transition metals, rhodium has been shown to be the best metal for selective conversion of syngas to oxygenated products like alcohols.^[7-9] It appears that rhodium's unique activity for oxygenate products likely stems from the intermediate position of its d-electron relative to metals that do not dissociate CO (Ir, Pd, Pt) and thus favor methanol production and those that easily dissociate CO under reaction conditions (Co, Fe) and, therefore, favor production of higher hydrocarbons.^[10–12] However, the majority of CO hydrogenation studies using unpromoted Rh have observed a strong selectivity for methane with minimal selectivity to oxygenates.^[13, 14] It is now well established that the addition of promoters as additives will greatly improve the catalytic performance of Rh catalysts resulting in moderate selectivities for specific oxygenates such as ethanol.^[15-17] In this work, we focus on one such promoter, Mn, to examine if a better, more intimate promotermetal interaction can increase the rate of reaction and the selectivity for higher alcohol production.

Among the most common methods in producing the promoted catalyst is impregnation of the promoter, which can be classified as dry (incipient wetness) or wet impregnation. In incipient wetness impregnation (IWI), a sufficient amount of metal solution is added to just fill the pore volume of the catalyst support or supported catalyst. However, this often results in poor to moderate interaction between active metal and promoter because the promoter will be randomly distributed across the surface of the support. Therefore, a key design objective is to increase the promoter-metal interaction to maximize its effectiveness. One possibility for potential improvement of the promoter-metal interaction is the use of the strong electrostatic adsorption (SEA) method, which has been refined by Regalbuto et al.^[18, 19] following Schwarz's original proposal about the electrostatic interactions between a metal ion and a charged support.^[20,21] The method of synthesis relies upon the naturally occurring hydroxyl groups (-OH) on the oxide surfaces that can become protonated or deprotonated when the contacting solution is acidic or basic, respectively. The density of the charged hydroxyl groups on the oxide at a given pH depends on its point of zero charge (PZC, the pH at which the hydroxyl groups remain neutrally charged). Metal oxides with a basic PZC (such as AI_2O_3 , its PZC is \approx 8.5) will have greater density of protonated hydroxyl groups (-OH2+) in acid environment (solution) and will adsorb anionic complex or metal precursor and vice versa. This can be expanded to preferential adsorption of a promoter on the metal oxide of the active metal at a pH at which it will not adsorb substantially on the support. In this study, MnO₄⁻ is selectively adsorbed on Rh_2O_3 , which has a high PZC (\approx 8.75) under acidic pH in the presence of the SiO₂ support, which has a low PZC (\approx 4). A schematic of the process is depicted in Figure 1.



Figure 1. Schematic of the selective adsorption of Mn promoters onto supported rhodium catalysts in acidic solution.

In the subsequent characterization, STEM and electron energy loss spectroscopy (EELS) were employed to observe the degree of metal-promoter interaction. In addition, X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) methods were used to investigate the information on the oxidation state and local geometry around the atom. Temperature-programmed reduction (TPR) was also used to study the reduction behavior of the promoted catalysts. Finally, the catalysts were tested in a plug flow reactor to determine the catalytic performance, that is, the rate and product selectivity. The results demonstrate higher ethanol selectivity with increasing metal-promoter interactions.

Results and Discussion

Permanganate adsorption

The permanganate adsorption results are shown in Figure 2. The data reveal that the amount of permanganate adsorbed



Figure 2. Permanganate adsorption survey on pure SiO_2 support (\bullet) and SiO_2-supported Rh₂O₃ (\blacksquare).

onto SiO₂ support was negligible in the uptake survey pH range. In comparison, if rhodium oxide (Rh₂O₃) was present on silica support, a considerable amount of Mn was absorbed on to the catalysts at acidic pH. This experimental observation is consistent with the previous results of Feltes et al.,^[22] who observed Mn uptake on TiO2-supported Co catalysts using the same strategy of preferential adsorption (the PZC of TiO₂ is 3.7, the PZC of Co_3O_4 is 8). Specifically, at an initial pH of 1 the maximum Mn uptake on 3%Rh/SiO₂ is about 3μ molL⁻¹ (\approx 4.5 wt%), and 1 wt% (0.67 μ molL⁻¹) Mn uptake occurred if the initial pH was shifted to 2.3. Moreover, at extremely low pH, both the pre- and post-concentrations of permanganate solution decreased dramatically after a certain time and the concentration difference in between the pre- and post-solutions was almost zero. This observation implies that redox reactions occurred at extremely low pH (below pH 0.5), the speciation of KMnO₄ occurs in an acidic solution through the following pathways [Eqs. (1) and (2)]:

 $MnO_4^{-} + 8 H^+ + 5 CI^- \rightarrow Mn^{2+} + 2.5 CI_2 + 4 H_2O$ (1)

$$MnO_4^{-} + 4 H^+ + 3 CI^- \rightarrow MnO_2 + 1.5 CI_2 + 2 H_2O$$
 (2)

If the initial pH dropped below 0.5, precipitation of a brown solid (MnO_2) was observed and therefore catalyst synthesis at these conditions was avoided.

In comparison with Mn promotion of Co/TiO₂ Fischer– Tropsch catalysts,^[22] there were similar trends for Mn adsorption onto the catalysts: there was almost no Mn uptake onto pure titania support, but if Co oxide was present in the catalyst, significant uptake was observed between pH 0.5 and 2.5. The Mn uptake reached a maximum at a pH of approximately

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1, just as we observed in the $\mathsf{MnRh}/\mathsf{SiO}_2$ system presented here.

Characterization of Mn-promoted Rh-based alcohol synthesis catalysts

Ertl and Freund^[23] proposed a maximum in the CO dissociation rate was reached in particles of approximately 3–4 nm, particles smaller or larger would lead to lower dissociation rate. As the synthesis of larger hydrocarbons (i.e., $C_xH_yO_z$; x > 1) in the CO hydrogenation reaction requires an initial CO dissociation before catalysis can proceed, it is implied that this same particle size should maximize the reaction rate. Previously, Hanaoka et al.^[24] have studied the effect of Rh particle size on CO hydrogenation products over Rh/SiO₂ catalyst. The authors found that as the Rh particle size increased, the overall products (oxygenates, hydrocarbons, etc.) from dissociated CO increased, but the portion of C₂ oxygenates decreased. A good balance in between these two functions can be achieved in a particle size range of approximately 3 nm. Therefore, we aimed at a particle size of approximately 3 nm in this study.

The dark-field STEM imaging of Mn-promoted Rh catalysts on SiO_2 are shown in Figure 3. The Rh particles exhibited small



Figure 3. Dark-field STEM imaging of $1 \% Mn_{SEA} 3\% Rh/SiO_2$ catalyst.

particle sizes (high dispersion). The particle size distribution analysis is shown in Figure 4 with an average particle size of the catalyst promoted by SEA of 2.8 ± 0.5 nm.

In addition to STEM imaging, EXAFS was used to confirm the average particle size. The magnitude of the Fourier trans-

form of the EXAFS spectra of the Rh catalysts are plotted in Figure 5 along with that of a Rh foil as a reference. All three samples have a large central peak at approximately 2.5 Å with a smaller shoulder at approximately 1.8 Å indicating that the particles are metallic. In Table 1, we summarize the average particle sizes obtained by EXAFS and STEM for our promoted and unpromoted catalysts. The similarity of the EXAFS data indicated that the average Rh particle size of the three catalysts is very close and the estimated size from the coordination number is approximately 2–3 nm, consistent with the STEM particle size and close to the optimal size reported in Ref. [23]. The Rh catalysts promoted by the SEA





Figure 4. Particle size distribution of $1 \, \text{Mn}_{\text{SEA}} 3\% \text{Rh/SiO}_2$ catalyst, note that the particle sizes distribution chart here was made by analyzing many dark field images similar to the image shown above.



Figure 5. Magnitude of the Fourier transform of the EXAFS ($k^2 = 2.5$ – 12.5 Å⁻¹) of Rh species present in the 3 wt %Rh/SiO₂ series of catalysts plotted with appropriate standards. —: Rh foil, —: 3 %Rh/SiO₂, —: 1 %Mn_{SFA}3%Rh/SiO₂, —: 1 %Mn_{WI}3%Rh/SiO₂.

Table 1. Particle size distribution of catalysts obtained by EXAFS and STEM.											
Catalyst	Coordination number ^[a]	Bond length ^[a] [Å]	$\sigma^{\rm 2[b]}$	Particle EXAFS [nm]	size STEM [nm]						
1 %Mn _{sea} 3 %Rh/SiO ₂	7.6	2.68	0.001	2.8 ± 0.3	2.8±0.5						
1 %Mn _{iwi} 3 %Rh/SiO ₂	6.5	2.67	0.001	1.9 ± 0.2	2.0 ± 0.4						
3 %Rh/SiO ₂	8.2	2.69	0.001	3.2 ± 0.3	2.7 ± 0.5						
[a] Value obtained from EXAFS data fitting; [b] Disorder in the neighbor distance in EXAFS data fitting.											

method are slightly larger than those promoted by the IWI method from both the EXAFS and STEM results even though the Rh particles were the same size prior to promotion. The unpromoted Rh catalyst has an average size determined by EXAFS of 3.2 ± 0.3 nm, which is almost the same as the average size for the catalyst promoted by the SEA method (\approx 2.8 nm), but bigger than the one promoted using the IWI method (\approx 1.9 nm). The reason for this is likely owing to the fact that the solution environments were different during promoter preparation (SEA was performed in acidic solution and IWI in deionized water) and therefore some redistribution of the metal may occur leading to different particle sizes. In summary, the particle sizes we obtained from EXAFS data, which represent the bulk average, are in agreement with the sizes we observed from the STEM data, which show the particle size distribution on a local scale.

EELS mapping has previously been used to analyze the distribution of the promoter phase on the catalyst surface.^[25] In Figure 6, we show the EELS mapping of Mn-promoted Rh/SiO_2



Figure 6. EELS elemental mapping of a) $1\%Mn_{WI}3\%Rh/SiO_2$ catalyst exhibiting intimate promoter–active metal interactions and b) $1\%Mn_{SEA}3\%Rh/SiO_2$ catalyst. **■**: Mn, **■**: Rh, **■**: silica.

catalysts (by SEA and IWI), the Mn K-edge energy loss signal is used to locate the Mn composition, O K-edge energy loss signal is used to locate the support position, and the mass contrast imaging was used for Rh signals, because the Rh Kedge signal is not sufficient for EELS spectrum image analysis. As seen in Figure 6 (a) for IWI samples, the promoter is not strongly associated with the metallic Rh particle, which is not surprising because through the IWI preparation method the Mn promoter was deposited randomly onto the catalyst without any special attraction with the Rh metal. On the other hand, the EELS mapping of our SEA-promoted catalyst (Figure 6b) exhibited a greater degree of promoter–active metal interaction, which is consistent with our initially proposed schematics (Figure 1) in catalyst preparation by the SEA method to achieve the selective Mn adsorption onto the Rh metal. In other words, this result suggests the creation of intimate interactions between Rh and Mn, which is believed to be the active sites for alcohol synthesis reaction, if we selectively directed the Mn promoter onto the supported Rh catalysts.

XANES measurements after in situ reduction at 210 °C reveal spectra (Figure 7) characteristic of metallic Rh for all the catalysts. Rh foil and rhodium oxide were used as standard referen-



Figure 7. XANES spectrum of Rh K-edge of 1 wt% Mn promoted 3 wt% Rh/ SiO₂ catalysts plotted with appropriate standards: Rh₂O₃ reference (-----), 1 %Mn_{SEA}3%Rh/SiO₂ catalyst (-----), 1 %Mn_{IWI}3%Rh/SiO₂ catalyst (-----), 3 %Rh/ SiO₂ catalyst (-----), and Rh foil reference (-----).

ces. Therefore, we can conclude that no matter how we add the promoters to the Rh catalysts, the Rh oxide present in the unreduced catalyst is reduced to metallic Rh after reduction. However, as shown by TPR, the reduction behavior of IWI- and SEA-promoted catalysts are different.

The TPR results for these catalysts are plotted in Figure 8. At first glance, the major reduction for unpromoted Rh/SiO₂ was observed at around 50 °C, which corresponds to the reduction from Rh₂O₃ to metallic Rh. The low reduction temperature of rhodium oxide is consistent with that reported elsewhere.^[26] For both the Mn-promoted Rh catalysts (those prepared by both IWI and SEA methods), Rh is completely reduced at low temperature, although the IWI-prepared catalyst has a slightly



 $\label{eq:Figure 8. TPR results of the 3 % Rh/SiO_2 catalyst (----), 1 % Mn_{SEA} 3 % Rh/SiO_2 catalyst (----), and 1 % Mn_{WI} 3 % Rh/SiO_2 catalyst (----).$

higher reduction temperature than the SEA-prepared catalyst. The TPR spectrum for the SEA prepared catalyst also exhibits a minor peak at approximately 200°C. This small peak at 200 °C likely stems from the reduction of manganese oxide from a higher oxidation state (MnO₂) to a lower oxidation state (most likely MnO, as Mn₂O₃ is very unstable). Reduction to metallic Mn requires a reduction temperature above 1000°C,^[27] so the formation of metallic Mn (which could alloy with Rh) is highly improbable and the Rh EXAFS spectra (Figure 5) do not indicate the presence of the bimetallic RhMn nanoparticles either. In the case of the promoted catalyst prepared by use of IWI to deposit Mn, we see the major reduction temperature shift to a higher temperature (≈ 100 °C), and the H₂ consumption decreased. This observation indicates that the way Mn interacted with Rh by IWI method makes it more difficult for Rh to be fully reduced. In other words, depositing promoters by SEA appears to have resulted in a higher degree of dispersion of the Mn species.

Alcohol synthesis reactivity results

The catalytic data is summarized in Table 2. Consistent with previous reactivity results, the unpromoted Rh/SiO₂ catalyst does not produce any oxygenates (including ethanol). The selectivity to higher hydrocarbons (the reaction produced \approx 30% methane and \approx 70% light hydrocarbons) was higher than that typically reported by Burch and Petch.^[9] For example, they tested a 2%wt Rh supported on silica catalyst for CO hydrogenation at 20 bar, 270 °C and a 1:1 syngas ratio, and obtained a methane selectivity of 48%, a light hydrocarbon selectivity of approximately 22%, and the remaining 30% share of the products contained primarily acid and acetaldehyde (which we did not observe in the products). The reaction pressure and temperature were almost identical to those in our system, but their H₂/CO ratio of 1:1 decreased the amount of H₂ available and increased the CO partial pressure, which could shift the product distribution. In recent work by Haider et al.^[28] a 2 wt% Rh catalyst supported on silica tested for CO hydrogenation at 20 bar, 300 °C, and a 1:1 syngas ratio, gave a 51% selectivity towards methane, and a light-hydrocarbon selectivity of approximately 47% with no other products reported. In general, our result is consistent in product distribution with that by Haider et al. (only methane and light hydrocarbon were detected).

Both promoted catalysts produced ethanol as well as acetaldehyde, methane, C_{3+} light hydrocarbons, acids, and C_{3+} oxygenates. The SEA-promoted catalysts exhibited significantly higher (\approx 3–4 times) ethanol selectivity than the IWI-promoted catalyst at each CO conversion (this trend is also presented in Figure 9). Moreover, at high CO conversion (>25%) both the SEA and IWI promoted catalysts began to produce other products such as propanol, ethane, propylene, and CO₂, which are not reported in Table 2. For example, at 40% CO conversion, the total production of these miscellaneous products summed to 5% for the SEA-prepared catalyst whereas these products amounted to 25% of the total products for the IWI-prepared catalyst.
 Table 2. Conversion of syngas over promoted and unpromoted Rh catalysts supported on silica.

Catalyst	CO conv. [%] ^[a]	TOF [s ⁻¹] ^[b]	E ^[a,c] [%]	A ^[a,d] [%]	М ^[а,е] [%]	L ^[a,f] [%]	O ^[a,g] [%]
3%RhSiO ₂	4.3	1.6	-	-	30	70	-
1 %Mn _{sea} 3 %RhSiO ₂	6.8 8.3 11.0 13.2 18.2 24.5 36.4 45.0	41.2 39.0 43.4 36.9 41.2 41.2 41.2 36.9	19.1 18.0 18.0 20.4 17.8 17.8 14.6 14.3	15.2 12.5 10.0 8.7 7.1 5.0 3.3 3.9	41.0 40.3 44.1 37.0 42.5 47.3 52.3 50.2	4.8 5.8 6.6 6.4 6.0 6.8 1.8 1.6	20.0 23.6 21.9 27.6 26.6 23.0 25.0 18.1
1 %Mn _{iwi} 3 %RhSiO ₂	7.5 8.8 10.8 14.5 19.0 27.0 42.0	29.2 27.8 27.8 27.8 29.2 30.1 32.1	4.8 5.3 4.5 5.8 6.0 5.6 5.0	8.4 8.4 7.5 7.6 7.6 3.6 2.5	17.5 19.9 20.6 23.6 23.2 16.7 20.5	51.2 49.2 50.6 46.5 46.9 28.9 18.8	18.1 17.3 16.9 16.6 16.4 33.0 28.5

[a] The CO conversions were calculated by using nitrogen gas as the internal standard, and the equation:

CO Conversion [%] = $(M_{CO feed} - M_{N_2 feed}/M_{N_2 product} M_{CO product})/M_{CO feed} 100\%$ in which M_i is the mole percent of component i. The selectivity to product i is based on the total number of carbon atoms among the total products and is defined as:

Selectivity_i [%] = $(n_i M_i)/(\Sigma n_i M_i)$ 100 %

in which n_i is the number of carbon atoms and M_i is the mole percent of product i detected downstream. [b] The TOF is calculated as the active sites per second of 1 g Rh, the Rh particles were assumed semispherical shape with the radius obtained from EXAFS size, the Rh atoms were assumed closed-packed cluster (diamond) with distance obtained from EXAFS bond lengths. [c] Selectivity for ethanol; [d] Selectivity for acetaldehyde; [e] Selectivity for methane; [f] Selectivity for light hydrocarbons C_{3+} ; [g] Selectivity for acetic acids and C_{3+} oxygenates.



Figure 9. Ethanol selectivities at various CO conversion points for the 1%Mn_{SEA}3%Rh/SiO₂ catalyst (•) and 1%Mn_{IWI}3%Rh/SiO₂ catalyst (•).

The improvement in selectivity for the SEA-promoted catalyst over the IWI-promoted catalyst suggests that more intimate interaction of the Mn promoter with Rh increases the higher-alcohol selectivity. This is consistent with the previous proposal that the active sites for the CO hydrogenation to

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higher alcohols reaction are located at the interface of the active metal and the promoter.^[15] In our catalysts synthesis, such an intimate promoter-active-metal interactions have been created by the SEA method so that there should be many more active sites available than for the catalysts prepared by the IWI method. The SEA catalyst also has a higher TOF than the IWI catalyst, which further indicates that stronger promoter-active-metal interactions improve the reaction rate for CO hydrogenation. From Table 2, it is observed that at lower conversion range (< 10%) higher concentrations of acetaldehyde are produced, which suggests that the acetaldehyde has not been fully hydrogenated to ethanol, and acetaldehyde is likely an intermediate product. If we take the ratio of ethanol/acetaldehyde for the two promoted catalyst at various CO conversion, there is always a higher ethanol/acetaldehyde ratio observed for the SEA-promoted catalysts suggesting Mn promotes the hydrogenation rate to give more ethanol. However, the SEA-promoted samples also produced approximately 20% more methane, which is the primary unwanted byproduct for this reaction; and the IWI-promoted samples, on the other hand, produced higher amounts of C_{3+} light hydrocarbons (\approx 40% more). The IWI-promoted catalyst prevented the complete hydrogenation of the dissociated CO to form large quantities of methane just like SEA-promoted catalyst did during the reaction process, but instead allowed more carbon insertion to form C_{3+} light hydrocarbons. In addition, both kinds of the promoted catalysts produced noticeable amount (\approx 15-30%) of acids and some higher oxygenates (primarily acetic acid). In the work by Hu et al.^[16] on CO hydrogenation reaction by using a Mn-promoted Rh catalyst supported on silica, at 39% CO conversion their primary products were ethanol (${\approx}54\,\%$ selectivity) and methane (${\approx}40\,\%$ selectivity). In addition, they produced trace amounts of CO_2 , methanol, and C_{3+} light hydrocarbons but did not quantify the formation of individual products such as ethane, and propane. The temperature in their reaction is similar (280°C) to that used in the current study, but Hu et al used a much higher pressure at 5.4 MPa (54 bar). In comparison, at a CO conversion of 45%, our major products from the SEA-promoted catalyst looked very similar to the products distribution from Hu et al. with major products as ethanol (14%) and methane (50%) and trace amounts of CO_2 , propanol, and C_{3+} light hydrocarbons. The SEA-promoted catalyst also produced significant amounts of acetic acid and C_{3+} oxygenates (25%), which were not seen in Hu et al.'s work. The higher alcohol production is likely a result of the much higher pressure used in their work and which likely leads to higher CO coverage on the catalytic surface. However, the authors did not report their reaction products at low CO conversion. In contrast, Hanaoka et al.^[24] studied the CO hydrogenation (260 $^{\circ}$ C, 20 bar, and 1:1 CO/H₂ syngas ratio) by using Mn-promoted Rh/SiO₂ (1:1 Mn/Rh molar ratio, 1 wt % Rh) catalyst at low CO conversion (0.5%) with product distribution approximately 13% selectivity towards ethanol, approximately 43% to methane, approximately 9% to methanol, approximately 23% to acetic acid, and approximately 36% to C₂ oxygenates. Comparing these results to our results at low CO conversion, our SEA catalyst gave higher selectivity to ethanol production, and produced approximately the same amount of methane and acetic acid. Unlike Hanaoka et al. we did not observe any methanol formation but instead formation of noticeable amounts of light hydrocarbons (5%) and acetaldehyde (15%). Most recently, Huang et al.^[29] found that very high selectivity to C_{2+} oxygenates with a maximum of 74.5% at 270 °C and 30 bar total pressure (1:2 CO/H₂) ratio could be achieved for Mn-promoted Rh nanoparticles encapsulated in a mesoporous silica nanoparticle framework (1.6 wt % Rh, 0.8 wt% Mn). Similar to our SEA-promoted catalyst, the primary C₂₊ products were acetaldehyde and ethanol and neither methanol nor CO₂ was observed. The selectivity to methane reported by Huang et al. is lower than that presented here (only 25% as opposed to \approx 40% at 10% conversion), but this may be a result of the higher pressure used by Huang et al., because this is also known to improve oxygenate selectivity and reduce methane production.^[13, 30, 31] Although the synthesis strategy is different, Huang et al. note that the improved selectivity is tied to an intimate relationship between the Rh nanoparticles and Mn promoter.

Conclusions

Herein, Mn was selectively deposited by strong electrostatic adsorption (SEA) onto Rh oxide, which upon reduction created an intimate promoter-active-metal interaction in the catalyst. By means of various characterization methods and CO hydrogenation reaction tests, the method of promoter addition was shown to be critical to the catalyst performance, because Mnpromoted Rh catalysts using the SEA method to add the Mn promoter were vastly more ethanol-selective than those using incipient wetness impregnation (IWI) to add Mn. Therefore, one can conclude that it is critical for targeted alcohol production to create a strong interaction between the active metal and promoter. Higher alcohol synthesis catalysts can be prepared by controlling the charging parameters of the active metal and support to selectively direct the promoter onto the active metal to achieve this intimate interaction. Furthermore, the selective adsorption method can be applied on other supports (TiO₂, Al₂O₃, etc.) and other promoters (V, La, etc.) to achieve the ideal metal-promoter interactions. For example, one can utilize the point-of-zero-charge difference between TiO₂ (≈ 5) and Rh₂O₃ (8.75) to direct any anionic precursor onto the Rh metal and enhance the metal-promoter interaction. Thus, significant potential exists for improvement of catalyst selectivity.

Experimental Section

Adsorption experiments

The supported Rh_2O_3 on SiO_2 (Aerosil 300, BET surface area = 330 m²g⁻¹, pore volume = 2.7 mLg⁻¹, the BET data was measured on a Micromeritics ASAP 2020 at liquid nitrogen temperature by N_2 adsorption) was synthesized through IWI method by using rhodium nitrate, $Rh(NO_3)_3$ (Sigma-Aldrich, 10% Rh in >5 wt% HNO₃). The precursor was dissolved in deionized water and then added dropwise to impregnate the support. The weight loading of Rh

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was controlled as 3 wt%. The catalyst was dried in air at RT for 24 h followed by calcination at 500 °C for 4 h (5 °C min⁻¹ ramp) to convert the rhodium nitrate into rhodium oxide, Rh₂O₃. The PZC of SiO₂ was determined by measuring the equilibrium pH at a high-oxide surface loading (10000 m²L⁻¹) after SiO₂ has been in contact with solutions of varying initial pH, the resulting PZC of SiO₂ was 4. Owing to the expense of pure Rh₂O₃, the PZC and [MnO₄]⁻ uptake experiments had to be modified. The PZC of Rh₂O₃ was determined by single-point analysis from 1 g Rh₂O₃·5H₂O (99.99%, Alfa Aesar) that was calcined at 350 °C for 4 h followed by copious washing in 0.01 \times HNO₃ and deionized water to remove any impurities. The resulting PZC=8.75 was measured using an Accumet spear-tip electrode at the point of incipient wetness with deionized water (pH_i=6.0).

Equilibrium adsorption experiments of the promoter were performed at a surface loading of 1000 m²L⁻¹ in excess liquid to prevent large shifts in the solution pH caused by the oxide buffering effect.^[32] The pH-adjusted solutions of KMnO₄ were contacted with SiO₂, and Rh₂O₃/SiO₂, and shaken for 1 h on a shaking bed, after which approximately 8 mL of filtered solution were analyzed for Mn concentration by using a PerkinElmer Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Mn uptake was determined as the difference in concentration between the preand post-contacted solutions (in both adsorption experiments, the surface loading was controlled as $1000 \text{ m}^2 \text{L}^{-1}$, and a $200 \text{ mg} \text{L}^{-1}$ Mn, permanganate solution was used). After the determination of the optimal uptake pH, the 3 %Rh₂O₃/SiO₂ catalyst was loaded with 1 wt% of Mn according to the adsorption experiments described above by using solutions with various pH and KMnO₄ as metal precursor. After filtration, the catalyst was dried overnight in the air at RT and then calcined at 350 °C for 4 h. For the purpose of comparison, 1 wt % Mn using Mn(NO₃)₂ as the precursor was also put onto the 3%Rh/SiO₂ catalyst by the IWI method.

Characterization

Scanning transmission electron microscopy (STEM) imaging was performed by using an aberration-corrected, cold-field emission gun microscope, JEOL JEM-ARM200CF, equipped with a postcolumn electron energy loss (EEL) spectrometer, and operated at 200 keV primary energy. For high-angle annular dark-field imaging (HAADF), a spatial resolution of more than 70 pm can be achieved, whereas the energy of 350 meV is possible for EEL spectroscopy. Herein, we used HAADF imaging to determine the particle size distribution. The chemical composition of the catalyst particles was determined by using EELS spectrum imaging combined with mass contrast signals.

Transmission X-ray absorption spectroscopy (XAS) of the Rh Kedge of the in situ reduced Rh/SiO₂ series catalysts were measured at Argonne national Laboratory's (Argonne, IL) Advanced Photon Source (APS) on the Materials Research Collaborative Access Team's (MRCAT) bending magnet beamline in sector 10-BM. Catalysts samples were pressed into an in situ cell and reduced at 210 °C in H₂. After cooling to RT, the sample chamber was filled with He prior to measurements. The data fitting was done with the software WinXAS 97, version 3.0. A Rh foil was used as a reference for both XANES and EXAFS fitting ($N_{Bh-Rh} = 12$, R = 2.69 Å).

Temperature-programmed reduction (TPR) experiments were performed on a Micromeritics Autochem 2920 using a thermal conductivity detector (TCD) detector. After baseline stabilization, the reduction was performed in a 10% H₂/Ar flow at a heating ramp of 10°C min⁻¹.

CO hydrogenation reaction

Alcohol synthesis reactions of the SiO₂-supported Rh catalysts were investigated under isothermal plug flow conditions achieve by diluting the catalyst (0.15 g) with SiC (0.3 g, 70 mesh) in a half-inch diameter stainless steel reactor. Catalysts were reduced prior to reaction for 1 h at 300 °C in H₂ (\approx 15% H₂ balanced in Ar). Reactions were performed at 20 bar, 285 °C and a syngas flow ranging from 15 mLmin⁻¹ to 110 mLmin⁻¹ to compare the catalytic performance of all the catalysts at different CO conversions. The syngas feed had a composition of 32% CO, 64% H₂ (a 1:2 CO/H₂ ratio) and 4% N₂ as an internal standard. The catalyst bed temperature was monitored by a thermocouple inserted within the catalyst bed. The reaction results reported here were generally obtained after 6 h reaction on-stream. A HP 6890 gas chromatograph equipped with one flame ionization detector (FID) and a TCD was integrated downstream of the reactor to analyze the reaction products. A 30 m by 0.32 mm ID HP-Wax bonded polyethylene glycol capillary column (made by Restek) was used for analysis of the organic products (i.e., ethanol, acetaldehyde, propanol, acetic acid, etc.) through FID. Light inorganic gases (H $_{\rm 2}$ CO, CO $_{\rm 2}$ N $_{\rm 2}$ etc.) and methane as well as light hydrocarbons were separated on packed columns and quantified with TCD.

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Keywords: alcohols · hydrogenation · manganese · rhodium · scanning probe microscopy

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