Rh-Based Mixed Alcohols Catalysts: A Computational Study on the Effect of Carbon vs Silica Supports

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Introduction
For several years, we have been involved in the optimization of Rh-based catalysts for biomass-derived syngas conversion into mixed alcohols. Rh-based catalysts are of interest because they are capable of high C₂⁺ oxygenate space-time yields (STYs) with the oxygenated products mainly comprised of ethanol, acetaldehyde, acetic acid and ethyl acetate [1]. However, in order to be an economic process, the product selectivity towards hydrocarbon gases (mainly methane) needs to be reduced.

Earlier research in our group showed that catalysts containing Rh and Mn produced the best overall combination of high activity (STY) and selectivity to mixed oxygenates [2]. More recently we showed that addition of Ir to Rh-Mn catalysts further improved both the C₂⁺ oxygenate STY and the selectivity to mixed oxygenates [3]. Experiments have also shown that different supports (i.e. silica or carbon based) produce significantly different product slates when compared at similar relative and total concentrations of the three metals. Utilizing the results of extensive catalyst characterization of some of the earlier Rh-Mn and Rh-Mn-Ir catalysts, we used quantum chemical models to better study the influence of different supports on dispersed Rh-Mn and Rh-Mn-Ir particles.

Methods and Models
Characterization of select silica and carbon-supported catalysts was used to develop a nominal catalyst cluster size and composition for modeling. The catalysts are typically prepared with a single-step impregnation procedure using the incipient wetness technique. Reaction testing was typically conducted at 250°C to 325°C and 1,200 psig using a syngas containing a ~4% carbon dioxide, 4% nitrogen, and the balance carbon monoxide (CO) and hydrogen (H₂) in a 1:8:1 ratio. TEM analysis of fresh and reduced catalysts with a nominal gross catalyst composition was ~1:0.0:0.6:0.1 Rh:Mn:Ir (if Ir was present), showed that the catalyst particles diameters lie typically in the range in 2-5 nm, although bigger particles were observed on both supports. XRD and XPS data of the reduced catalysts suggested that Rh and Ir were reduced to metals on both supports. The oxidation state of Mn could not be as clearly determined due to significant overlap of Mn oxidation states in the Mn 2p electron region.

The computer models assumed a 50 atom cluster, which satisfied this size range consisting of a range of Rh:Mn:Ir metal ratios that included the nominal catalyst composition. The particles were placed on two support models, an O-terminated α-quartz to represent the silica support and a single graphene sheet to represent the carbon support. Ab initio molecular dynamics (AIMD) simulations were performed with CP2K [4] within periodic boundary conditions. The systems were equilibrated at T=600K, and approximately 20 ps of simulation trajectories were used for the data analysis. Simulations were performed in vacuum as well as in the presence of H₂ and CO to model the syngas environment.

Results
Preliminary results from the AIMD analysis show that in high temperature the particles are very plastic, yet behave distinctly different on the two supports. On C-support the clusters are nearly spherical and highly mobile, Fig.1(a), with the C-Rh interaction being the strongest amongst the 3 metals, Fig.1(b), red. The C-Mn and C-Ir distributions imply diffuse interactions, with the possibility of Ir being preferentially segregated toward the interior of the cluster, Fig.1 (b), blue and green. The clusters on silica are more spread out than on C-support. The trajectories showed migration of Mn from the cluster to the silica support. Fig.1 (c), while some O atoms from the support also appeared to migrate onto the metal cluster, Fig.1 (d).

Significance
These results help explain the effects of different support on the catalyst behavior across a range of catalytic systems.

Figure 1. Snapshot from AIMD of C-supported Rh₄MnIr₄ particle (a), resulting pair distribution of C (support) and metal atoms (particle) (b). Two different views of the same composition particle on silica, showing Mn-migration on the support (c) and O-migration from the support on the particle.

References
4. CP2K is a program to perform atomistic simulations within a general framework of different methods, http://www.cp2k.org/.